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THE ZEEMAN EFFECT FOR THE ARC SPECTRUM OF GOLD

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ABSTRACT. The Zeeman effect for about 50 gold lines has been observed and recorded. The field strength used was about 23,000 gauss. A former assignment of terms to the Au I spectrum by McLennan and McLay has been verified to some extent, but certain modifications have been suggested. Suggestions have also been made as to the identity of a few terms which were not previously identified.

§ 1. INTRODUCTORY

PREVIOUS observations of the Zeeman effect for gold were made by Purvis in 1905*. He, however, made no measurements of the magnetic resolution of the lines, but merely indicated the type of splitting observed in the magnetic field.

The present work was undertaken after the publication of a paper on the Arc Spectrum of Gold by McLennan and McLay†. They were able to find a number of terms which were predicted by application of the Hund theory to complex spectra. The purpose of this paper is to show the agreements and discrepancies which have been observed between the measured Zeeman effects for the lines, and this former classification. Resolutions of nearly 40 of the stronger lines in the arc spectrum of gold have been observed and measured. Attempts have also been made to obtain patterns for the fainter lines, but the time of exposure necessary in some cases has been prohibitively great.

The estimated intensities of some of the lines, as given in McLennan's paper, were found to be discordant with the intensities as observed on our plates, and in such cases new intensities have been assigned.

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* Purvis, *Proc. Camb. Phil. Soc.* **13**, 82 (1905).

† McLennan and McLay, *Proc. Roy. Soc.* A. **112**, 95 (1926).

§ 2. OBSERVATIONAL DATA

In the present investigation photographs of the Zeeman effect for lines of Au I ranging from λ 2350 to λ 6280 have been taken. All the photographs were taken with a 10 ft. concave Rowland grating in an Eagle mounting. The apparatus employed in the production of the magnetic field was an electro-magnet of horse-shoe type, fitted with bored conical poles (semi-angle about 60°). Only small currents could be passed through the coils of the magnet, as it was not water cooled. For exposures of longer duration than about 30 minutes, a current of not more than 6 amp. was allowable, but for shorter periods currents up to 10 amp. were employed. The current through the magnetising coils was kept constant during an exposure by means of a carbon rheostat.

With the poles very close together (about 1 mm.), a maximum field strength of about 27,000 gauss was obtainable. Under these conditions, however, difficulty arose on account of arcing between the poles themselves. Field strengths of from 22,000–25,000 gauss (with poles 2–3 mm. apart), were much more satisfactorily attained and were generally used in the exposures.

Only an arc in air has been used as a source of light. Some plates were taken with an arc *in vacuo*, produced by the use of a vacuum chamber fitting around the poles, as described by Beals* in a paper on palladium, but no additional Zeeman components appeared, neither were the patterns more easily measured. Also, by the use of a vacuum arc, the necessary time of exposure was much increased, and in addition trouble was occasioned, since the gold electrodes had to be removed from time to time to be scraped and the vacuum chamber made this removal difficult. It was found that a periodic scraping of the electrodes assisted the arc to burn steadily.

The two arms of the magnet were insulated from one another and were made the positive and negative poles of the arc. In the earlier experiments one pole only was drilled along its axis. Through a brass collar fitted into this hole was threaded an iron rod, into the tip of which a small piece of gold was riveted. Another small piece of gold was fixed upon the solid pole piece of the undrilled arm. The arc was established between the gold pieces. In later experiments, however, both arms were drilled, and through a brass collar fitted into each arm passed an iron rod, with gold tip, as described above. This gave the advantage of the easy removal of both electrodes for scraping purposes, without disturbance of the inter-pole distance. The arc was run on 220 volts.

Difficulty was experienced in maintaining a steady arc between two gold electrodes. A small current had to be used, as otherwise the heat of the arc melted the gold. Two methods were adopted with a measure of success to render the arc steadier. In the first case, it was found that if small quantities of certain salts were fed into the arc at intervals it would burn without attention for a considerable period. The salts actually used were the chlorides of cadmium and calcium. In the second method, one gold and one silver electrode were used. Either of these methods served a double purpose, for, in addition to giving a more stable arc, they also gave lines on the plates exhibiting Zeeman resolutions suitable for use in calculating the field strength.

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* Beals, *Proc. Roy. Soc.* A. **109**, 369 (1925).

All lines except those of wave-length greater than λ 5100 were obtained in the third and higher orders. The time of exposure varied from 5 min., in the case of the very strong lines, to 2½ hours for the weak lines. With these long exposures it was found that nitrogen bands frequently appeared strongly on the plates, and masked the Zeeman effects of the fainter gold lines present in the band. In an attempt to overcome this difficulty the arc was run in an atmosphere of oxygen, but even after repeated attempts with long exposures some of the faint lines have never appeared on the plates. The time during which the current could pass through the magnetising coils was limited by the excessive heating of the coils and iron, with a consequent variation in field strength which blurred the Zeeman patterns.

All photographs were taken at right angles to the direction of the magnetic field. A quartz double-image prism was used to separate the oppositely polarised components of the patterns. The time of exposure when the quartz prism was used was greatly increased, and accordingly it was impossible to obtain the separated *p* and *s* components of some of the weak lines. In some instances a greater number of components was disclosed by its use. For example, the pattern for the line λ 5064·6 appeared as a very diffuse doublet without the prism, but with its use the pattern was observed to consist of eight components of type (0·79), 0·57, 1·14, 1·68.

Purvis used a gold spark as a source of illumination, and estimated the strength of field employed at 40,000 gauss. This is undoubtedly an over-estimate, for in certain cases he observed lines as merely broadened, whereas in the present investigation these same lines have been at least partially resolved. It is accordingly concluded that the field strength in this work is greater than that obtained by Purvis. It may also be noted here that whereas he gave the line λ 3586·70 as a doublet, or reversal, the present results have shown it to be a triplet of type (0), 1·08. This pattern is shown in the plate.

In most cases complete resolution of the lines into their Zeeman components has not been attained, but the measurements of the unresolved patterns have been helpful in deciding to what degree the classification of terms by McLennan and McLay has been verified. In a number of instances the effects have appeared as pseudo-triplets, or pseudo-quartets. By investigation of the type to which the pattern conforms, the *g*-values of some of the terms have been calculated. From these calculated values it has been possible, in some cases, to suggest modifications in the previous assignment of terms.

§ 3. THE FIELD STRENGTH

In order to calculate the field strength, measurements of Zeeman resolutions of the following lines have been used: the *H* and *K* lines of calcium, λ 3933·66 and λ 3968·46, giving resolutions (0·33), 1·00, 1·67, and (0·67), 1·33 respectively; the cadmium lines λ 5086·06, λ 4800·09 and λ 4678·37, giving resolutions (0, ·5), 1·0, 1·5, 2·0; (0·5), 1·5, 2·0; and (0), 2·0 respectively; and the silver lines λ 3280·66 and λ 3382·86, with resolutions (0·33), 1·00, 1·67 and (0·67), 1·33 respectively.

The field strength was calculated from the Lorentz formula:

$$H = d\lambda \,(\text{normal})/\lambda^2 . a,$$

where

$$a = 4{\cdot}7 \times 10^{-5}\ \text{cm.}^{-1}\ \text{gauss}^{-1}.$$

§4. NOTE ON NOTATION

Table 1 is a modified form of one given by McLennan and McLay* in their paper, and shows the most stable energy states of the gold atom which are involved in its emission spectrum. The system of notation is one which has been adopted by Fowler in his recent papers. Two "families" of terms are shown, each being based upon a definite condition of the core. The same prefix is assigned to all terms arising from the same electron configuration, and the orbital designation of the series electron is adopted as this prefix, which is printed in italics. For example, $6p\ {}^2P_1$ indicates the ${}^2P_1$ component due to an electron arrangement in which the moving electron occupies a 6_2 orbit. By the use of this prefix a term is completely specified, and so the use of the former dashed terms is unnecessary. Combinations between terms involving only a single electron shift are obtained by application of the ordinary selection rule for azimuthal quantum numbers to the series electron. Thus, a 6*s* term will combine with a 6*p*, but not with a 6*d* (subject, of course, to the inner quantum number restrictions).

Table 1

(*a*) Au 1

K L M N	O			P			Q	R	Electrons in unclosed groups	Adopted prefix	Terms	Series limit Au 1 term
$1_1 \dots 4_4$	5_1	5_2	$5_3 \dots$	6_1	6_2	$6_3 \dots$	$7_1 \dots$	$8_1 \dots$				
60	2	6	10	1					*s*	6*s*	${}^2S$	${}^1S$
60	2	6	10		1				*p*	6*p*	${}^2P$	${}^1S$
60	2	6	10			1			*d*	6*d*	${}^2D$	${}^1S$
60	2	6	10				1		*s*	7*s*	${}^2S$	${}^1S$
60	2	6	10					1	*s*	8*s*	${}^2S$	${}^1S$
60	2	6	9	2					d^9s^2	$6s''$	${}^2D$	${}^3D$
60	2	6	9	1	1				d^9sp	$6p''$	${}^4P\ {}^4D\ {}^4F\ {}^2P\ {}^2D\ {}^2F$ ${}^2P^1\ {}^2D^1\ {}^2F^1$	${}^3D$ ${}^1D$
60	2	6	9	1		1			d^9sd	$6d''$	${}^4S\ {}^4P\ {}^4D\ {}^4F\ {}^4G$ ${}^2S\ {}^2P\ {}^2D\ {}^2F\ {}^2G$ ${}^2S^1\ {}^2P^1\ {}^2D^1\ {}^2F^1\ {}^2G^1$	${}^3D$ ${}^1D$

(*b*) Au II

K L M N	O			P			Terms
$1_1 \dots 4_4$	5_1	5_2	$5_3 \dots$	6_1	6_2	$6_3 \dots$	
60	2	6	10				${}^1S$
60	2	6	9	1			${}^3D$ ${}^1D$

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* *Loc. cit.*

The combining properties of terms involving a double electron shift are governed by the azimuthal quantum number rule, $\Delta k = \pm 1$, for one electron, and $\Delta k = \pm 2$ or 0 for the other. These possibilities are indicated by dashing the electron symbols corresponding to the definite families, instead of dashing certain of the terms themselves. Intercombinations between the dashed and undashed terms then take place under the normal rules, for example, a p term may combine with a p', but not with a p'' term.

In the case of different sets of terms arising from the same electron arrangement but based upon a different state of the core, a numerical superscript is applied to the term symbol in order to distinguish the particular state of the core to which it is due. As an example, in the second family of terms shown in Table 1 we get two ^2D terms from the $6p''$ state of the series electron, one based upon the ^3D and the other upon the ^1D term of the Au II spectrum. To distinguish them, the one based upon the ^3D term of Au II is written ^2D, whereas the one derived from the ^1D term is written with a numerical superscript, thus $^2D^1$. This superscript in no way affects the combining properties of the terms.

§ 5. RESULTS

The measured Zeeman effects for the lines which have appeared on the plates are collected in Table 2. The wave-lengths are as given by McLennan and McLay in their paper on the gold arc spectrum. They are taken mainly from Kayser and Konen's *Handbook*, vol. 7, but a few lines were measured by Bloch, and a few of the very faint lines were measured by McLennan and McLay themselves. In several cases, however, new intensities have been assigned. It was found that the relative intensities of certain groups of lines were not correctly indicated by the assignment of intensities as given by McLennan and McLay in their paper. It should be borne in mind, however, that it is practically impossible to maintain the same scale of intensities throughout when the various members of a multiplet occur in such widely separated regions of the spectrum.

In Table 2 the observed Zeeman effect has been expressed in decimal fractions of the normal separation as shown by lines in a singlet system, and where the pattern exhibited asymmetrical splitting, this has been shown by placing the shorter and longer wave-length components to the left and right respectively of the undisturbed line. Such an asymmetrical pattern is shown in the plate for the line λ 2352·65. The components in parenthesis are those polarised in a direction parallel to the applied field. The strongest component of a pattern is denoted by a black figure. The theoretical Zeeman effects for the lines are also given, these being calculated on the assumption of the combination of terms involved as given in the last column of the table.

§ 6. DISCUSSION OF RESULTS

In the majority of cases the resolution has not been complete. In spite of this fact, it has been possible to indicate to what degree the former classification may be considered to be satisfactory, and in some instances the incompletely resolved patterns have made it possible to suggest a redistribution of terms.

Table 2

λ (I.Å.U)	Int.	ν (vac.)	Observed Zeeman effect	Calculated Zeeman effect	Suggested combination
7510·74	5	13310·6			$6p\ ^2P_2-7s\ ^2S_1$
6278·18	5	15923·8	(**0**), ·83	(·07), ·73, **·87**	$6s''\ ^2D_2-6p\ ^2P_1$
5956·98	3	16782·4			$6p''\ ^4D_4-6d''\ ^4D_4$
5862·94	1	17051·6			$6p''\ ^2D_3-6d''\ ^4D_3$
5837·40	6	17126·5	(·68), 1·31	(·67), 1·33	$6p\ ^2P_1-7s\ ^2S_1$
5721·26	0	17473·8			$6p''\ ^2P_2-6d''\ ^4D_3$
5655·76	2	17676·2	(0), 1·44	(**·03**, ·09, ·14), 1·28, 1·34, 1·40, 1·46, 1·51, **1·57**	$6p''\ ^4D_4-6d''\ ^4D_3$
5261·82	1	18999·6			$6p''\ ^2D_3-6d''\ ^4D_2$
5147·39	1	19421·9			$6p''\ ^2P_2-6d''\ ^4D_2$
5064·62	2	19739·4	(**·79**), ·57, 1·14, 1·68	(·27, **·80**), ·53, **1·07**, 1·60	$6s''\ ^2D_2-6p\ ^2P_2$
4811·61	3	20777·3	(**·72**), ·48, 1·02, 1·55	(·27, **·80**), ·53, **1·07**, 1·60	$6p\ ^2P_2-6d\ ^2D_2$
4792·60	8	20859·7	(**0**), 1·12	(**·07**, ·20), **1·00**, 1·13, 1·27, 1·40	$6p\ ^2P_2-6d\ ^2D_3$
4620·70	0	21635·7			$6p''\ ^4F_3-6d''\ ^4D_4$
4607·35	2	21698·4	(**0**), 1·22	(**·18**, ·54), **·83**, 1·19, 1·55, 1·92	$6p''\ ^4P_2-6d''\ ^4D_3$
4488·26	4	22274·1	(**·50**), ·99, 1·37, 1·69	(·10, ·29, ·48, **·67**), ·76, ·95, 1·14, **1·33**, 1·52, 1·72, 1·90	$6p''\ ^4F_4-6d''\ ^4D_4$
4437·28	1	22530·0	(**·58**), ·84, 1·34	(·17, ·51, **·86**), ·51, ·86, **1·20**, 1·54, 1·89	$6p''\ ^4F_3-6d''\ ^4D_3$
4315·11	4	23167·9	(**0**), 1·25	(**·07**, ·20, ·33), **·91**, 1·04, 1·17, 1·30, 1·43, 1·57	$6p''\ ^4F_4-6d''\ ^4D_3$
4241·84	2	23568·2	Six components equally spaced	(33), **1·00**, 1·67	$6p\ ^2P_2-8s\ ^2S_1$
4084·14	2	24478·1	(**0**), 1·07	(**·09**, ·26), **·77**, ·94, 1·12, 1·29	$6p''\ ^4F_3-6d''\ ^4D_2$
4065·08	8	24592·8	(**0**), ·87	(·07), ·73, **·87**	$6p\ ^2P_1-6d\ ^2D_2$
4040·95	4	24739·7	(0), 1·19	(**·11**, ·34), ·69, ·91, 1·14, **1·37**	$6s''\ ^2D_2-6p''\ ^4F_3$
3909·39	2	25572·2	(**·90**), 1·52	(·47, **1·40**), ·33, **1·27**, 2·20	$6s''\ ^2D_2-6p''\ ^4P_2$
3897·88	7	25647·7	(**0**), 1·26		$a\ -6d''\ ^4D_4$
3889·45	1	25703·3			$6p''\ ^4D_4-6d''\ ^4F_5$
3875·08	1	25800·8			$6p''\ ^4D_4-c$
3801·97	1	26294·7			$6p\ ^2P_2-7d\ ^2D_2$
3795·90	4	26336·7	Broadened, with central component	(**·07**, ·20), **1·00**, 1·13, 1·27, 1·40	$6p\ ^2P_2-7d\ ^2D_3$
3650·74	3	27383·8	(·68), 1·33	(·67), 1·33	$6p\ ^2P_1-8s\ ^2S_1$
3355·18	2	29796·1	·46	(·27, **·80**), ·53, **1·07**, 1·60	$6s''\ ^2D_2-6p''\ ^2P_2$
3320·14	4	30110·6			$6p\ ^2P_1-7d\ ^2D_2$
3308·31	4	30218·3	(**·24**, ·64), 1·46, **1·85**	(**·20**, ·60), ·60, 1·00, 1·40, 1·80	$6s''\ ^2D_2-6p''\ ^2D_3$
3204·74	3	31194·7	(**0**), 1·28	(**·05**, ·14, ·24, ·33), 1·00, 1·09, 1·19, 1·28, 1·38, 1·48, 1·57, **1·67**	$6p''\ ^4F_4-6d''\ ^4F_5$
3194·73	2	31292·5			$6p''\ ^4F_4-c$
3146·37	1	31773·5			
3122·78	9	32013·5	(**0**), 1·11	(**·07**, ·20), **1·00**, 1·13, 1·27, 1·40	$6s''\ ^2D_3-6p\ ^2P_2$
3029·22	8	33002·2	(**·83**), 1·64		$6s''\ ^2D_3-a$
2891·96	1	34568·5			$a\ -6d''\ ^4F_5$
2883·46	4	34670·4	(·51), —	(·20, **·60**), ·60, **1·00**, 1·40	$6s''\ ^2D_2-6p''\ ^4D_2$
2748·26	8	36375·9	(0), 1·33	(**·02**, ·06, ·10), 1·14, 1·18, 1·22, 1·26, **1·29**	$6s''\ ^2D_3-6p''\ ^4F_4$
2700·90	5	37013·7	(**·44**), 1·08	(·09, ·26, **·43**), ·77, ·94, **1·11**, 1·28, 1·44	$6s''\ ^2D_3-6p''\ ^4F_3$
2688·72	5	37181·4	1·27, (**0**), 1·17	(**·03**, ·09), ·77, ·83, ·89, **·94**	$6s''\ ^2D_2-6p''\ ^2F_3$
2675·95	10*R*	37358·8	(·67), 1·33	(·67), 1·33	$6s\ ^2S_1-6p\ ^2P_1$
2641·49	6	37846·1	1·17, (**0**), 1·01	(**·27**, ·80), **·40**, ·93, 1·47, 2·00	$6s''\ ^2D_3-6p''\ ^4P_2$
2590·05	4	38597·7			$6s''\ ^2D_2-7p\ ^2P_1$
2544·20	3	39293·4	·80	(·27, **·80**), ·53, **1·07**, 1·60	$6s''\ ^2D_2-7p\ ^2P_2$
2510·50	3	39820·6	1·74, **0**, 1·62	(**·29**, ·86), ·51, 1·08, 1·66, **2·23**	$6s''\ ^2D_2-6p''\ ^4D_3$
2427·98	10*R*	41174·0	Reversed. Six components equally spaced	(·33), **1·00**, 1·67	$6s\ ^2S_1-6p\ ^2P_2$
2387·75	4	41867·6	1·77, (0), 1·47	(**·11**, ·34, ·57), ·86, 1·09, 1·31, 1·54, 1·77, **2·00**	$6s''\ ^2D_3-6p''\ ^4D_4$
2376·25	3	42070·3	1·26, **0**, 1·45	(**·07**, ·20), **1·00**, 1·13, 1·27, 1·40	$6s''\ ^2D_3-6p''\ ^2P_2$
2364·57	3	42278·1	Broadened		$6s''\ ^2D_2-b$
2352·65	4	42492·2	1·34, 0, 1·03	(0), 1·20	$6s''\ ^2D_3-6p''\ ^2D_3$
2129·46	2	46945·4	Broadened	(0), 1·20	$6s''\ ^2D_3-6p''\ ^4D_2$
2126·62	2	47008·2			$6s\ ^2S_1-6p''\ ^4P_2$
2021·40	3 +	49454·6			$6s''\ ^2D_3-6p''\ ^2F_3$
*λ vac.					
1951·97	3 +	51230·3			$6s\ ^2S_1-6p''\ ^2P_2$
1939·24	2	51566·6			$6s''\ ^2D_3-7p\ ^2P_2$
1919·63	4	52093·4			$6s''\ ^2D_3-6p''\ ^4D_3$
1879·87	3	53195·2			
1833·14	3	54551·2			$6s''\ ^2D_3-b$
1665·73	0	60033·7			$6s\ ^2S_1-7p\ ^2P_1$
1646·66	0	60729·0			$6s\ ^2S_1-7p\ ^2P_2$

* Wave-lengths below λ 2000 are by E. W. H. Selwyn.

From incompletely resolved patterns, by a study of the intensity distribution among the components, the *g*-values of the terms involved have been calculated. It has been found that in most cases the *g*-values are abnormal (*i.e.* they do not conform to the Landé values). A similar departure from Landé values has been noted by Shenstone* in observations of the Zeeman effect for the copper arc. It is apparently due to the fact that the spectrum is partly of the second rank, *i.e.* it is produced by atoms having two electrons neither in *s*-orbits nor in closed groups.

In some cases where the patterns are resolved only as triplets, it has been instructive to resolve the pattern predicted by the use of Landé's *g*-values into a theoretical blend triplet. Since the distribution of intensities in a complicated pattern follows a quadratic formula, it is possible to assume the centre of gravity of the pattern to be approximately one-quarter of the way from the strongest to the weakest component. As an example, in the case of the combination $^2P_2$–$^2D_3$ the theoretical pattern is (**·07**, ·20) **1·00**, 1·13, 1·27, 1·40. This reduces to a theoretical blend triplet (0), 1·10 (approx.). The line λ 3122·78, in which these terms are involved, exhibits a pattern (0), 1·11.

For the sake of clearness, the combinations between the terms have been drawn up in the form of tables. The magnitudes of the terms are those given by McLennan and McLay, with the difference that here the deepest term, 6*s* $^2S_1$, has been given its absolute value, 74461·0 cm.$^{-1}$. This term was calculated by McLennan and McLay as the limit of the ^2P series, of which 6*p* ^2P and 7*p* ^2P are two consecutive members in Rydberg sequence.

Table 3 contains combinations between terms based upon a d^{10} state of the core (Table 1). In the same table are also shown the combinations between the terms 6*p*, 7*p* ^2P with 6*s*″ ^2D.

Table 3

Term	Term value	6*p* $^2P_1$ 37102·2	6*p* $^2P_2$ 33286·8	7*p* $^2P_1$ 14428·5	7*p* $^2P_2$ 13732·8
6*s* $^2S_1$	74461·0	37358·8 (10*R*)	41174·0 (10*R*)	60033·7 (0)	60729·0 (0)
7*s* $^2S_1$	19976·2	17126·2 (6)	13310·6 (5)		
8*s* $^2S_1$	9718·6	27383·8 (3)	23568·2 (2)		
6*d* $^2D_3$	12509·5	24592·8 (8)	20777·3 (3)		
6*d* $^2D_2$	12427·1		20859·7 (8)		
7*d* $^2D_2$	6991·9	30110·6 (4)	26294·7 (1)		
7*d* $^2D_3$	6950·1		26336·7 (4)		
6*s*″ $^2D_2$	53026·2	15923·8 (5)	19739·4 (2)	38597·7 (4)	39293·4 (3)
6*s*″ $^2D_3$	65300·2		32013·5 (9)		51566·6 (2)

In so far as measurements of the Zeeman effect have been made upon the lines in Table 3, the classification (due to McLennan and McLay) has been verified. As will be seen from Table 2, lines involving P → S, and P → D transitions give patterns which conform to the theoretical Zeeman effect. In the case of the lines λ 5064·62 (6*s*″ $^2D_2$–6*p* $^2P_2$) and λ 4811·61 (6*p* $^2P_2$–6*d* $^2D_2$) the resolution has been sufficiently complete to fix the nature of these terms without difficulty. The line λ 2544·20 ($6s''\ {}^2D_2$–$7p\ {}^2P_2$) gave a Zeeman effect which appeared as a doublet, 0·80, but this was doubtless due to the fact that it was photographed in the fourth order, and that it is in a region where the sensitivity of the plates is diminishing. Moreover, the lines λ 5065 and λ 4812, in each of which the transition ${}^2P_2$–${}^2D_2$ is involved, each gave the Zeeman effect as a doublet, 0·8, when the field was of a smaller intensity and when the polarising prism was not used. The lines λ 6278 and λ 4065 gave incompletely resolved triplets (0), 0·83 and (0), 0·87 respectively, whereas the theoretical blend triplet for ${}^2P_1$–${}^2D_2$ would be (0), 0·87. The pattern for the lines involving the terms ${}^2D_3$–${}^2P_2$ conform to the theoretical blend triplet (0), 1·10. The identity of the $6s''\ {}^2D$ term has thus been verified. The separation of the components of this term is 12274 wave-numbers, and this separation has recently been compared with the separation of the corresponding term in Cu I and Ag I by McLennan and McLay* in a paper on Au II. It has been shown that the separations are approximately proportional to the squares of the atomic numbers of the elements concerned.

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* Shenstone, *Phys. Rev.* **28** (3), 449 (1926).

Assuming the Landé g-values for the ${}^2P$ terms, the calculated g's of $6s''\ {}^2D_2$ and $6s''\ {}^2D_3$ are 0·79 and 1·24 respectively. The corresponding Landé values are 0·80 and 1·20. Unfortunately, only one combination of the term $6s''\ {}^2D_3$ with the ${}^2P$ terms has been observed in a magnetic field, and so it has been impossible to check the value 1·24 for $6s''\ {}^2D_3$. This value has been used to calculate the g's of terms in combination with it.

Table 4 contains combination lines between the terms arising from the states of the atom represented by $5d^9\ 6s^2$ and $5d^9\ 6s\ 6p$. It is in this table that a rearrangement of terms has been found necessary, since the observed Zeeman effects are not in agreement with the former classification.

Table 4

j of term	g of term	Term suggested	Term value	$6s''\ {}^2D_2$ 53026·2	$6s''\ {}^2D_3$ 65300·2	Term suggested by McLennan and McLay
2	1·14	$6p''\ {}^2P_2$	23230·1	29796·1 (2)	42070·3 (3)	${}^2P_2$
2	1·36	$6p''\ {}^4P_2$	27454·0	25572·2 (2)	37846·2 (6)	${}^2D'_2$
3	1·23	$6p''\ {}^2D_3$	22807·9	30218·3 (4)	42492·3 (4)	${}^2F_3$
2	1·14	$6p''\ {}^4D_2$	18355·8	34670·4 (4)	46945·4 (2)	a_{23}
3	1·15	$6p''\ {}^4D_3$	13205·6	39820·6 (3)	52093·4 (4)	c_{23}
4	1·35	$6p''\ {}^4D_4$	23432·6		41867·6 (4)	${}^4D'_4$
3	·97	$6p''\ {}^2F_3$	15844·8	37181·4 (5)	49454·6 (3 +)	b_{23}
3	·96	$6p''\ {}^4F_3$	28286·5	24739·7 (4)	37013·7 (5)	${}^2D'_3$
4	1·27	$6p''\ {}^4F_4$	28924·3		36375·9 (8)	${}^4F_4$
		a (${}^4P_3$?)	32298·0		33002·2 (8)	${}^2F_4$
		b	10748·4	42278·1 (3)	54551·2 (3)	d_{23}

Table 5

Term	Term value	$6p''\ {}^2P_2$ 23230·1	$6p''\ {}^4P_2$ 27454·0
$6s\ {}^2S_1$	74461·0	51230·3 (3 +)	47008·2 (2)

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* McLennan and McLay, *Trans. Roy. Soc. Can.* **22**, 103 (1928).

Table 5 gives two lines produced by combination of the deepest term of the spectrum, $6s\ ^2S_1$, with two of the terms of Table 4. McLennan and McLay gave a third line, λ 1879·13 ($\nu = 53198{\cdot}5$), as being a combination between $6s\ ^2S_1$ and another term of the $5d^9\ 6s\ 6p$ configuration. The magnitude of this other term was found by assuming λ 3146·37 ($\nu = 31773{\cdot}5$) to be produced by its combination with $6s''\ ^2D_2$. This gives the magnitude of the term as 21252·7 cm.$^{-1}$, which in combination with $6s\ ^2S_1$ gives $\nu = 53208{\cdot}3$. A new measurement of the former λ 1879·13 is given by Selwyn as λ 1879·87 (in vaxus), with $\nu = 53195{\cdot}2$. The discrepancy between these observed and calculated wave-numbers is thus 13, which is much too great for λ 1879·87 to be justly claimed as the combination in question. It has accordingly been omitted. The inclusion of λ 3146·37 in Table 4 then becomes a speculation, and has also been omitted. The term 21252·7 cm.$^{-1}$ may have no real significance.

McLennan and McLay suggested that the lines λ 2748·26 ($\nu = 36375{\cdot}9$) and λ 2387·75 ($\nu = 41867{\cdot}6$) involved the terms $^4F_4$ and $^4D_4$ in combination with $^2D_3$, but they were uncertain as to which was the deeper term. The present work has shown $^4F_4$ to be deeper than $^4D_4$. From the Zeeman pattern obtained for the line λ 2748 a g-value of 1·27 for $6p''\ ^4F_4$ has been calculated. The Landé g is 1·24. The calculated g-value for $6p''\ ^4D_4$ is 1·35, and the Landé g is 1·43. It is considered that two other components of the $6p''\ ^4D$ term are also present in combination with $6s''\ ^2D$, these being $6p''\ ^4D_3$ (13205·6 cm.$^{-1}$) and $6p''\ ^4D_2$ (18355·8 cm.$^{-1}$). Assuming this classification, the $6p''\ ^4D$ term is seen to be partially inverted. The relative intensities of the lines in question support this classification. The calculated g-values for $^4D_3$ and $^4D_4$ are 1·15 and 1·14 respectively, whereas the Landé values for these terms are 1·37 and 1·20 respectively. There has been no check on this value for $^4D_3$, since the magnetic resolution of only λ 2510·50 ($\nu = 39820{\cdot}6$), itself a faint and rather nebulous line, was obtainable. The line λ 1919 is in a region inaccessible to Zeeman measurements.

The term 28286·5 cm.$^{-1}$ has been designated as $6p''\ ^4F_3$, having a g-value of 0·94 (Landé value, 1·03). The intensities of the lines formed by the combination $6p''\ ^4F_{3,\,4}$ with $6s''\ ^2D$ support this arrangement.

The j of the term 23230·1 must be 2 or 3, since it combines with both $^2D_2$ and $^2D_3$. This present investigation has shown that the Zeeman effect for λ 3355 ($\nu = 29796{\cdot}1$) is a faint pseudo-doublet, and λ 2376 ($\nu = 42070{\cdot}3$) is a triplet. Hence the j of the term must be 2. The calculated g is 1·14, and the term is given as $6p''\ ^2P_2$, which is in agreement with the former classification by McLennan and McLay. Similarly, the j of the term 27454·0 must be 2, since λ 3909 ($\nu = 25572{\cdot}2$) exhibits a pseudo-quartet (·90) 1·52 (indicating that the j's of the combining terms are equal), and λ 2641 ($\nu = 37846{\cdot}1$) exhibits a triplet (0) 1·09 (indicating unequal j's). The calculated g of the term is 1·36. It is suggested that the term involved may be $6p''\ ^4P_2$. If this is so, then Table 5 shows two lines produced by combination of $6p''\ ^2P_2$ and $6p''\ ^4P_2$ with $6s\ ^2S_1$.

In the case of the term 22807·9 the magnetic resolution of the lines produced by combination of this term with $6s''\ ^2D$ has been sufficiently complete to decide its nature fairly definitely as $6p''\ ^2D_3$. The pattern for the line λ 3308 ($6s''\ ^2D_2$–$6p''\ ^2D_3$) is reproduced in Plate 1. The calculated *g*-value for the term $6p''\ ^2D_3$ is 1·23, as compared with the Landé value 1·20. McLennan and McLay formerly classified this term as $^2F_3$, but the observed Zeeman effects do not conform to this view. A calculated *g* of 0·97 for the term 15844·8, which must have a *j*-value of 3, from consideration of the type of Zeeman effect, suggests the probability of its being $6p''\ ^2F_3$.

Special attention is drawn to the term 32298·0. The line λ 3029 ($\nu = 33002·2$) gives a Zeeman effect which has been measured as (**0·83**), 1·64. The pattern in question is reproduced in Plate 1. It is seen to be quite definitely a pseudo-quartet, from which it appears that the term 32298·0 should have a *j* equal to 3, since only combinations between terms of equal *j* give pseudo-quartets. Assuming this value of *j*, the calculated *g* of the term is 1·57, which would indicate $6p''\ ^4P_3$. In opposition to this view is the fact that no combination of this term with $6s''\ ^2D_2$ has been found, whereas if the term is actually $^4P_3$ it should occur quite strongly, and would be in an easily observed region. Further evidence against a *j*-value of 4 is obtained by observation of the Zeeman effect for λ 3898 ($\nu = 25647·7$), in Table 6, which is produced by combination of this same term with one of value 6650·2. This latter term has been fairly definitely fixed as $6d''\ ^4D_4$. Hence if the *j* of the term 32298·0 were 4, the Zeeman effect should be a pseudo-quartet, whereas it was observed as a triplet (**0**), 1·26, which points to the inequality of the *j*'s of the combining terms. The observed triplet is in agreement with the assumption of the transition $6p''\ ^4P_3$–$6d''\ ^4D_4$. McLennan and McLay gave the term as being $^2F_4$, but this does not agree with the observed Zeeman patterns. The combination $^2D_3$–$^2F_4$ should give a blend triplet (0), 1·07 (approx.), whereas the observed pattern was (**0·83**), 1·64, as previously stated.

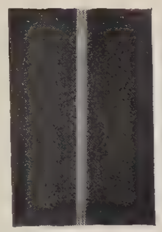
No observations of the Zeeman effect for the lines $\nu = 42278·1$ and $\nu = 54551·2$ have been possible, and so it is impossible to suggest the identity of the term 10748·4.

Table 6 shows combinations between $6p''$ terms and $6d''$ terms. McLennan and McLay did not suggest the identity of these $6d''$ terms. From a consideration of the magnetic resolutions exhibited by lines in this table, the suggestions are made that the term 6650·2 is represented by $6d''\ ^4D_4$ (*g*-value = 1·41, Landé $g = 1·43$), and 5756·4 by $6d''\ ^4D_3$ (*g*-value = 1·25, Landé $g = 1·37$). By observation

Table 6

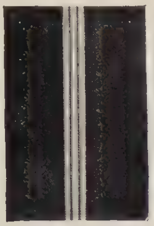
Term	Term value	$6d''\ ^4D_4$ 6650·2	$6d''\ ^4D_3$ 5756·4	$6d''\ ^4D_2$ 3808·3	$6d''\ ^4F_5$ − 2270·5	*c* − 2368·2
$6p''\ ^2P_2$	23230·1		17473·8 (0)	19421·9 (1)		
$6p''\ ^4P_2$	27454·0		21698·4 (2)			
$6p''\ ^2D_3$	22807·9		17051·6 (1)	18999·6 (1)		
$6p''\ ^4D_4$	23432·6	16782·4 (3)	17676·2 (2)		25703·1 (1)	25800·8 (1)
$6p''\ ^4F_3$	28286·5	21635·7 (0)	22530·0 (1)	24478·1 (2)		
$6p''\ ^4F_4$	28924·3	22274·1 (4)	23167·9 (4)		31194·7 (3)	31292·5 (2)
a	32298·0	25647·7 (7)			34568·5 (1)	

(*a*)



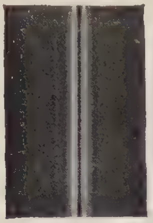
Au λ 2352·65
1·34, 0, 1·03

(*b*)



Au λ 2748·26
(0), 1·33

(*c*)

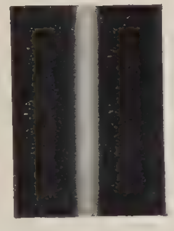


Au λ 3029·22
(·83), 1·64

(*d*)

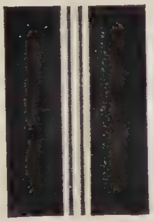
Au λ 3308·31
(·24, ·64), 1·46, 1·85

(*e*)



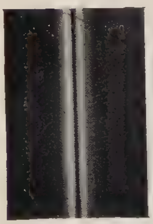
Au λ 3586·70
(0), 1·08

(*f*)



Au λ 4315·11
(0), 1·25

(*g*)

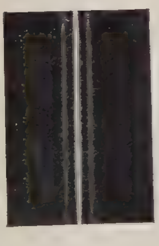


Au λ 4437·28
(·58), ·84, 1·34

(*h*)

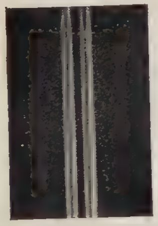
Au λ 4488·26
(·50), ·99, 1·37, 1·69

(*k*)



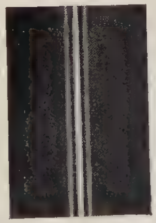
Au λ 4607·35
(0), 1·22

(*l*)



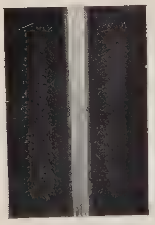
Au λ 5837·40
(·68), 1·31

(*m*)



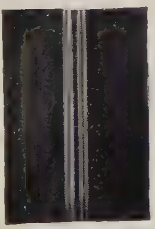
Au λ 6278·18
(0), ·83

(*n*)



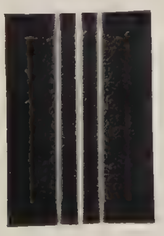
Ca λ 3933·66
(·33), 1·00, 1·66

(*o*)



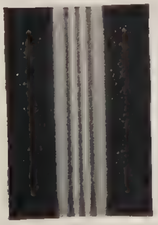
Ag λ 3382·86
(·66), 1·33

(*p*)



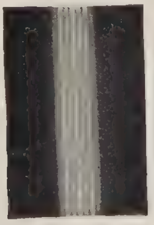
Cd λ 4678·37
(0), 2·00

(*q*)



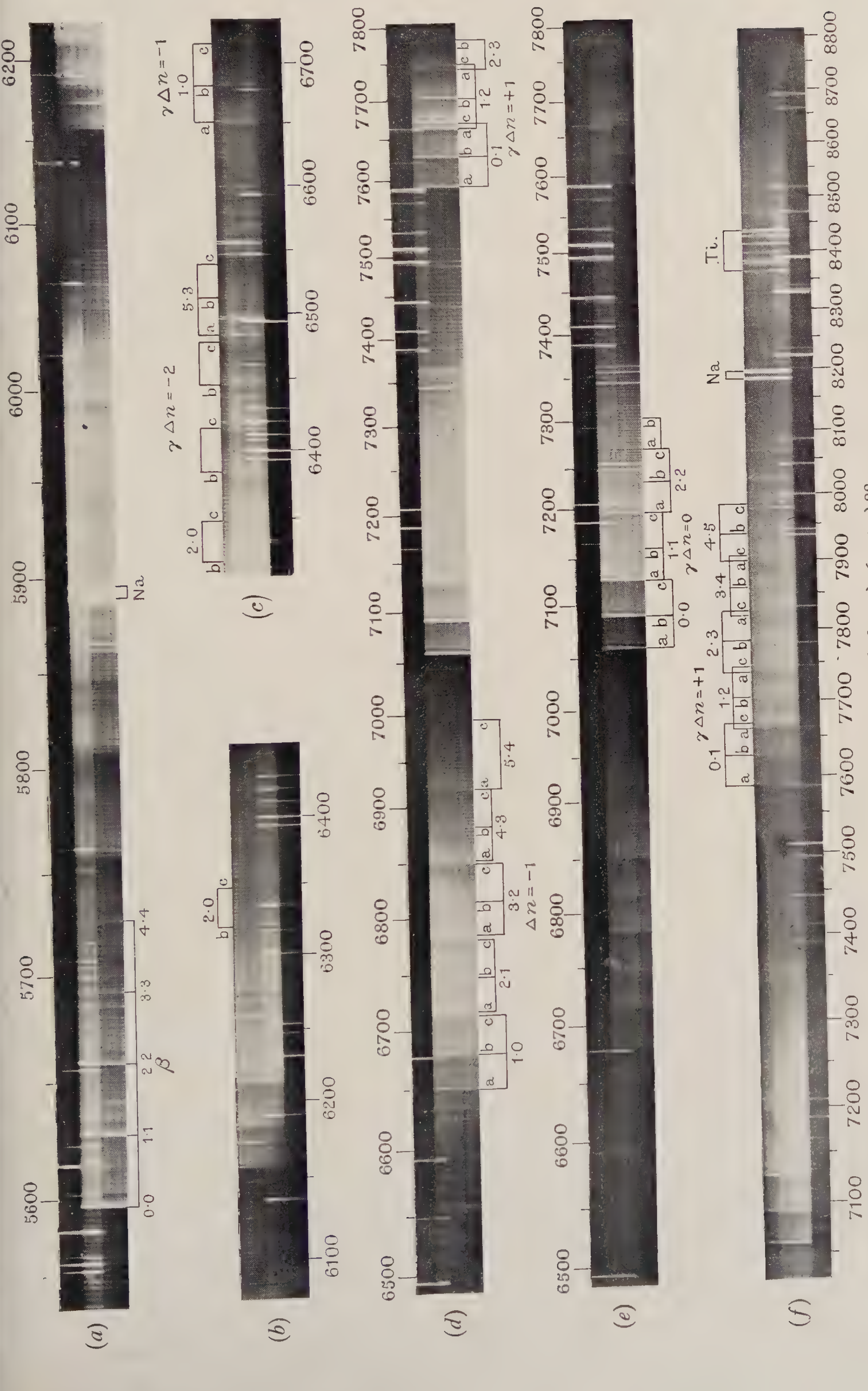
Cd λ 4800·09
(·50), 1·50, 2·00

(*r*)



Cd λ 5086·06
(0, ·50), 1·00, 1·50, 2·00

Some typical Zeeman patterns.



Titanium oxide bands from λ5600 to λ8800.

of the Zeeman effect for λ 4084 ($\nu = 24478·1$) it is suggested that the term 3808·3 is probably $6d''\ {}^4D_2$. The term − 2270·5 appears to have a *j*-value of 5, and the assignment of $6d''\ {}^4F_5$ to this term is in reasonably good agreement with the observed effect for λ 3205 ($\nu = 31194·7$), which is (**0**), 1·28, whereas the theoretical blend triplet would be (0), 1·48. Owing to the faintness of the other lines involving the term − 2270·5, their magnetic resolutions have not been observable, and so the identity as $6d''\ {}^4F_5$ is in some doubt. No line involving the term designated *c* has appeared on the Zeeman effect plates, and so no suggestion is offered for it.

§ 7. SOME GOLD SPARK LINES

In Table 7 are collected a number of lines which have appeared on the Zeeman effect plates of the gold arc but are not directly attributable to Au I. They are apparently spark lines, and probably arose from the regions near the poles of the arc, which were necessarily very close together. Some of these lines, namely those marked with an asterisk, have been assigned to the Au II spectrum by McLennan and McLay†. The wave-lengths and estimated intensities are from Kayser and Konen. The Zeeman effect is expressed in the usual manner.

Table 7

λ (I.A.U.)	ν (vac.)	Observed Zeeman effect
5230·31 (1*n*)	19114·0	(0) 1·17
4902·27 (1)	20393·0	(0) ·86
*4052·80 (6)	24667·4	(**0**) 1·05
*4016·07 (5)	24892·9	(0) 1·04
3915·86 (1)	25530·0	1·08
3874·68 (3)	25801·3	(0) 1·09
*3803·99 (6)	26280·8	(0) 1·33
*3633·25 (4)	27515·2	(0) 1·19
3607·50 (1*n*)	27712·2	(0) 1·34
3553·56 (3)	28132·8	1·41 (**0**) 1·28
3586·70 (5)	27872·9	(0) 1·08
*3122·50 (5)	32016·4	(0) 1·19
3034·13 (1)	32948·8	(0) 1·22
*2990·26 (5)	33432·2	·86
*2913·51 (10)	34312·8	(**0**) 1·19

* Classified as Au II lines by McLennan and McLay.

§ 8. ACKNOWLEDGMENT

In conclusion the authors wish to express their indebtedness and sincere thanks to Prof. A. Fowler, F.R.S., who suggested the investigation, and who has taken an unfailing interest during its progress.

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† McLennan and McLay, *Trans. Roy. Soc. Can.* **22**, 103 (1928).

PRESSURE SHIFTS IN THE SPECTRUM OF IONISED NITROGEN

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Abstract: The shifting of certain lines in the spectrum N II caused by a change in pressure of the gas in the discharge tube has been investigated. Over 80 lines within the region λ 6800–λ 1850 have been found to shift, and the amount of shift for most of these lines has been determined. The shift is in all cases in the direction of increasing wavelength. The shifts have been discussed in relation to the terms giving rise to the lines concerned and the results have facilitated the identification of three new singlet terms. An enquiry into the nature of the effect leads to the conclusion that it is in the main a Stark effect.

§ 1. INTRODUCTORY

It has been observed by Fowler* that certain groups of lines in the spectrum of singly ionised nitrogen, N II, show a broadening and a large shift ($>$ 0·5 Å.) towards the red when the spectrum is obtained from a vacuum discharge through a capillary tube, the gas being at a pressure of a few cm. of mercury. The wavelengths from which the shifts were reckoned were those obtained when the pressure of the gas was very low. The effect seemed to call for further investigation, inasmuch as it appeared to be confined to but a small fraction of the spectrum and was remarkable also for the magnitudes of the shifts compared with those usually associated with the "pressure effect." A similar instability in certain groups in the spectra of O II† and O III‡ has also been observed by Fowler.

A more extensive examination of the spectrum of N II has revealed many more lines subject to shift at higher pressures, and the results raise some points of interest. A preliminary investigation into the nature and cause of the effect has also been made.

§ 2. EXPERIMENTAL

The spectrum was obtained from an electric discharge through nitrogen in an ordinary H-type tube having a capillary about 8 cm. long and 1 mm. bore. The tube was excited by a 12 in. induction coil with mercury interrupter. In series with the discharge tube was connected a spark gap the electrodes of which were two brass spheres about 1 cm. in diameter. The distance between the spheres could be varied by a screw adjustment: for most of the photographs this distance was kept at

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* *Proc. Roy. Soc.* A. **107**, 37 (1925).

† *Proc. Roy. Soc.* A. **110**, 478 (1926).

‡ *Proc. Roy. Soc.* A. **117**, 325 (1928).

3·0 mm. A condenser, the capacity of which could be varied but was kept constant for a particular series of photographs, was in parallel with the secondary terminals of the coil.

The method adopted for detecting the shifts was to take two photographs, one at a fairly high pressure (about 5 cm.) and the other at low pressure ($< 0·1$ cm.), in juxtaposition on the same plate. In this way the shifted lines could be readily picked out. For determining the magnitudes of the shifts, the high pressure was finally chosen to be about 1 cm. This was necessary in order that measurements might be made on close groups, the members of which at higher pressures fused into one another. Although the adoption of this comparatively low pressure made the quantity to be measured smaller, the loss was to a considerable extent compensated for by the increased accuracy in the settings on the lines, due to their comparative sharpness at the lower pressure. In fact it was found that the percentage error involved in measuring the small shifts was of the same order as for the large shifts.

Photographs were taken over the region λ 6800–λ 1850, in most cases with adequate dispersion and resolving power. A large dispersion was not always to be desired as the shifted lines became increasingly broad and the error arising from this cause counterbalanced any advantage due to increased dispersion. As it was not possible to photograph the whole of the region λ 6800–λ 1850 at the same time, it was necessary to ensure that shifts in different regions should be strictly comparable. The range was accordingly divided into the following intervals: (i) λ 6800–λ 3800; (ii) λ 4000–λ 2900; (iii) λ 3100–λ 2400; (iv) λ 2800–λ 2250; (v) λ 2300–λ 1850; so that two overlapping regions had a shifting group common to both. For example, the unstable group common to (i) and (ii) was that at λ 3800; to (ii) and (iii) the singlet at λ 3007. It was then assumed that if the group at λ 3800 showed the same amount of shift on plates (i) and (ii) the conditions under which the spectrum was emitted in each case were the same and all other groups on the two plates could be compared directly with one another.

Region (i) was photographed chiefly on a glass prism instrument having a dispersion of 29 Å./mm. at λ 6600 and 5 Å./mm. at λ 3800. (ii), (iii) and (iv) were photographed on a quartz instrument of the Littrow type (Hilger's E. 1) giving a dispersion of 12 Å./mm. at λ 4000 and 2 Å./mm. at λ 2300. For (v) a small quartz spectrograph by Bellingham and Stanley, with a mean dispersion of about 7 Å./mm., was used.

All the lines of N II which have been found to shift are given in Table I together with the amount of shift. In all cases the shift is to the red.

§ 3. DESCRIPTION OF TABLE I

The wave-lengths and classifications are those published by Fowler and Freeman*. The notation has been changed to that adopted more recently by Fowler† in his paper on O III. In this notation a term may be generally represented in the form $nk^{r}\mathrm{T}_{j}$, where nk represents the orbit of the series electron giving

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* *Proc. Roy. Soc.* A. **114**, 664 (1927).

† *Proc. Roy. Soc.* A. **117**, 317 (1928).

Table 1. Shifts in lines of N II

λ (Int.)	Classification	$d\lambda$	$d\nu$
6836·2 (1)	$3d\,^3P_1 - 4p\,^3S_1$	·87	1·8
6812·26 (2)	$P_2 - S_1$	·86	1·8
*6630·5 (2)	$3d\,^1P_1 - 4p\,^1S_0$	·43	1·0
6545·2 (0)	$3d\,^3D_3 - 4p\,^3D_2$ $D_1 - D_1$		
6533·0 (1)	$D_2 - D_2$		
6522·3 (0)	$D_1 - D_2$		
6504·9 (2)	$D_3 - D_3$	·70	1·6
6492·0 (0)	$D_2 - D_3$		
†6357·0 (3)	$3d\,^3D_{12} - 4p\,^3P_{01}$	·54	1·3
†6347·1 (1)	$D_1 - P_1$		
†6340·67 (4)	$D_3 - P_2$	·44	1·1
†6328·6 (1)	$D_2 - P_2$	·45	1·1
*6242·52 (5)	$3d\,^1F_3 - 4p\,^1D_2$		
‡6173·40 (3)	$3d\,^3F_3 - 4p\,^3D_2$	·50	1·3
‡6170·16 (1)	$F_2 - D_1$		
‡6167·82 (4)	$F_4 - D_3$	·65	1·7
§6150·9 (0)	$F_2 - D_2$	·70	1·8
§6136·9 (0)	$F_3 - D_3$	·50	1·3
5104·45 (2)	$3p\,^1S_0 - 4s\,^1P_1$	·56	2·2
4227·83 (3*n*)	$3p\,^1P_1 - 4s\,^1P_1$	·40	2·3
‡3856·07 (3)	$3p\,^3P_2 - 4s\,^3P_1$	·37	2·5
‡3855·08 (2)	$P_1 - P_0$	·40	2·7
3847·38 (3)	$P_1 - P_1$	·33	2·2
3842·20 (3)	$P_0 - P_1$	·34	2·3
3838·39 (5)	$P_2 - P_2$	·33	2·2
3829·80 (3)	$P_1 - P_2$	·32	2·2
3615·88 (1)	$3p\,^3S_1 - 4s\,^3P_0$	·30	2·3
3609·09 (2)	$S_1 - P_1$	·30	2·3
3593·60 (3)	$S_1 - P_2$	·27	2·1
3331·32 (3)	$3p\,^3D_2 - 4s\,^3P_1$	·23	2·1
‖3330·30 (2)	$D_1 - P_0$		
‖3328·79 (4)	$D_3 - P_2$		
3324·58 (2)	$D_1 - P_1$	·22	2·0
3318·14 (2)	$D_2 - P_2$	·28	2·5
3006·86 (7)	$3p\,^1D_2 - 4s\,^1P_1$	·20	2·2
2897·49 (3*n*)	*A*		
2892·86 (4*n*)			
2885·25 (6*n*)			
2884·25 (2*n*)			
2879·73 (4*n*)			
2877·66 (2*n*)			
2823·67 (4)		·06	0·8
*2799·20 (4)	$3p\,^1P_1 - 4d\,^1D_2$	·16	2·1
2735·0 (1*n*)	$3p\,^1S_0 - 5s\,^1P_1$		
2709·82 (6)			
2590·91 (4)		·12	1·7
2524·55 (1)	$3p\,^3P_2 - 4d\,^3D_2$	·13	2·1
‡2522·51 (1)	$P_1 - D_1$		
‡2522·27 (4)	$P_2 - D_3$	·17	2·7
2520·85 (3)	$P_1 - D_2$	·14	2·2
2520·27 (2)	$P_0 - D_1$	·14	2·2
2496·88 (4)	$3p\,^3P_2 - 4d\,^3P_2$	·15	2·4
2494·02 (1)	$P_2 - P_1$	·15	2·4
§2493·22 (0)	$P_1 - P_2$	·14	2·3
2490·37 (2)	$P_1 - P_1$	·13	2·1
2488·82 (1)	$P_1 - P_0$	·14	2·2
2488·21 (0)	$P_0 - P_1$		
2461·30 (3)	$3p\,^1P_1 - 5s\,^1P_1$	·35	5·8
2390·90 (2)	$3p\,^3S_1 - 4d\,^3P_2$	·18	3·1
2388·24 (1)	$S_1 - P_1$	·18	3·2
2386·80 (0)	$S_1 - P_0$		
§†2321·62 (1)	$3p\,^3D_3 - 4d\,^3F_3$	·09	1·7
§†2319·90 (1)	$D_2 - F_2$	·09	1·7
‡†2317·01 (3)	$D_3 - F_4$	·08	1·5
‡†2316·66 (1)	$D_1 - F_2$		
‡†2316·46 (2)	$D_2 - F_3$		
2293·40 (2)	$3p\,^3P_2 - 5s\,^3P_1$ $3p\,^3D_3 - 4d\,^3D_2$		
2292·72 (1)	$P_1 - P_0$		
2291·67 (2)	$D_3 - D_3$		
2290·31 (1)	$P_1 - P_1$		
2288·47 (3)	$P_0 - P_1$ $D_2 - D_2$	·17	3·2
2286·73 (4)	$P_2 - P_2$ $D_1 - D_1$ $D_2 - D_3$	·26	4·9
2283·70 (2)	$P_1 - P_2$	·27	5·2
*2206·10 (3)	$3p\,^1D_2 - 4d\,^1D_2$ $3p\,^3S_1 - 5s\,^3P_0$		
2203·72 (1)	$S_1 - P_1$		
2197·58 (2)	$S_1 - P_2$		
2096·79 (3)	$3p\,^3D_2 - 5s\,^3P_1$		
2096·16 (2)	$D_1 - P_0$		
2095·47 (6)	$D_3 - P_2$		
2094·12 (2)	$D_1 - P_1$		
2091·20 (3)	$D_2 - P_2$		
*1990·99	$3p\,^1D_2 - 5s\,^1P_1$		
*1886·82 (4)	$3s\,^1P_1 - 4p\,^1S_0$		
*1877·97 (2)	$3s\,^3P_1 - 4p\,^1S_0$		
*1868·50 (1)	$3s\,^1P_1 - 4p\,^1D_2$		

* Classified by author. In the case of λ 2206 the original classification of Fowler and Freeman, $3p\,^3S_1 - 5s\,^3P_0$ is adopted in part. The additional combination yielding a line in this position explains the anomalous intensities in the triplet.

† Recently classified by L. J. Freeman to whom the author is indebted for the use of unpublished results.

‡ Not very well resolved at high pressure.

‖ Confused with band lines.

§ Very faint at high pressure.

A. Unclassified multiplet.

rise to the term (*e.g.* $3s$, $3p$, $3d$; the letters s, p and d representing the azimuthal quantum numbers 1, 2 and 3); r is the multiplicity, T the term type (S, P, D, etc.) and j the inner quantum number. For instance, a triplet P term arising from a 3_2 orbit would be represented by $3p\ {}^3P_{012}$.

The relation of the earlier to the present notation is therefore as follows:

$1\ {}^3P_{012}' = 3s\ {}^3P_{012}$
$1\ {}^1P_1' = 3s\ {}^1P_1$

$1\ {}^3P = 2p\ {}^3P$
$1\ {}^1D_2' = 2p\ {}^1D_2$
$1\ {}^1S_0' = 2p\ {}^1S_0$

$2\ {}^3P' = 4s\ {}^3P$
$2\ {}^1P_1' = 4s\ {}^1P_1$

$3\ {}^3P' = 5s\ {}^3P$
$3\ {}^1P_1' = 5s\ {}^1P_1$

$1\ {}^3D_{123}' = 3p\ {}^3D_{123}$
$2\ {}^3P = 3p\ {}^3P$
$1\ {}^3S_1' = 3p\ {}^3S_1$
$2\ {}^1D_2' = 3p\ {}^1D_2$
$1\ {}^1P_1 = 3p\ {}^1P_1$
$2\ {}^1S_0' = 3p\ {}^1S_0$

$2\ {}^3D' = 4p\ {}^3D$
$3\ {}^3P = 4p\ {}^3P$
$2\ {}^3S_1' = 4p\ {}^3S_1$
$3\ {}^1D_2' = 4p\ {}^1D_2$
$2\ {}^1P_1 = 4p\ {}^1P_1$
$3\ {}^1S_0' = 4p\ {}^1S_0$

$1\ {}^3F_{234}' = 3d\ {}^3F_{234}$
$1\ {}^3D = 3d\ {}^3D$
$1\ {}^3P''' = 3d\ {}^3P$
$1\ {}^1F_3' = 3d\ {}^1F_3$
$1\ {}^1D_2 = 3d\ {}^1D_2$
$1\ {}^1P_1''' = 3d\ {}^1P_1$

$2\ {}^3F' = 4d\ {}^3F$
$2\ {}^3D = 4d\ {}^3D$
$2\ {}^3P''' = 4d\ {}^3P$
$2\ {}^1F_3' = 4d\ {}^1F_3$
$2\ {}^1D_2 = 4d\ {}^1D_2$
$2\ {}^1P_1''' = 4d\ {}^1P_1$

It will be observed that most of the lines which shift have been classified, the chief exception being the group marked A. Unfortunately this group is very diffuse even at low pressures and although a shift could be seen with the unaided eye no measurements have yet been made. The remaining lines are probably singlets: further reference to these will be made later.

In some instances the amount of shift is given for only a few members of a multiplet. This was largely due to the fact that at the high pressure the line spectrum was always accompanied by a faint continuous spectrum and as the shift was accompanied by a broadening of the lines some of the fainter lines became practically undistinguishable against the continuous background and in any case would not allow of measurement. No measurements have yet been made on any of the lines below λ 2290. This was due partly to the small separations of the members of the multiplets and partly to the small amount of shift in Å. units.

It will be observed that in cases where the lines of a multiplet are well separated the shifts of the separate lines are equal within the limits of experiment.

§ 4. THE TERM SHIFT

It has been found that all lines arising from transitions between orbits for which $n \leqslant 3$ (*i.e.* the value of n in the general term $nk\,{}^rA_j$) are steady as far as could be detected by the method employed, while all lines associated with orbits for which $n > 3$ are unsteady. It seems reasonable on this evidence to assume that orbits for which $n \leqslant 3$ are themselves stable (or at most affected to a small and equal extent) and that the orbits for which $n > 3$ are the ones affected. The only transitions so far observed involving $n > 3$ are $n = 5$ to $n = 3$ and $n = 4$ to $n = 3$, the transition $n = 5$ to $n = 4$ being outside the range of wave-lengths here investigated. Assuming the terms having $n \leqslant 3$ to be stable, it follows that the shift of any of the lines here considered will represent the amount by which the upper term is affected. This we may conveniently call the "term shift." It is unfortunate that the observable transitions are so limited as the measurement of shifts, in lines arising from orbits for which $n = 4, 5, 6$, etc., combining with others for which $n > 3$, would provide a valuable check on the assumption that the shift is a property of the terms and also on the actual values of the term shifts. For instance, $4p\,{}^3S_1$–$5s\,{}^3P_1$ would involve two unsteady terms, the lower of which shows a shift of 1·8 cm.$^{-1}$ while the upper shows a shift of 5·2 cm.$^{-1}$. This line should therefore show a shift of 5·2 cm.$^{-1}$ – 1·8 cm.$^{-1}$ = 3·4 cm.$^{-1}$.

In the case of a multiplet, the average of the shifts of the separate lines is taken as the term shift, those lines for which measurements are less accurate being omitted in arriving at the average. The fact that no systematic variation of shift in the different members of a multiplet has been detected shows that if there is any variation of term shift with inner quantum number it must be small.

As the shift is to the red in all cases, the change corresponds to an increase in the term value, the deepest term being assumed to have the highest value. That is, it corresponds to a depression of the electron level such as would be caused by a shrinking of the orbit.

Table 2. Term shifts

Term	$d\nu$ (i)*	$d\nu$ (ii)†	Ratio (ii)/(i)
$4s\,{}^3P$	2·2	4·6	2·1
$4s\,{}^1P$	2·2	4·4	2·0
$4p\,{}^3D$	1·6		
$4p\,{}^3P$	1·2		
$4p\,{}^3S$	1·8		
$4p\,{}^1D_2$	2·2		
$4p\,{}^1S_0$	1·0		
$4d\,{}^3F$	1·6		
$4d\,{}^3D$	2·2	4·1	1·9
$4d\,{}^3P$	2·3	4·6	2·0
	3·1	5·8	1·9
$4d\,{}^1D_2$	2·1		
$5s\,{}^3P$	5·2		
$5s\,{}^1P$	5·8	11·5	2·0

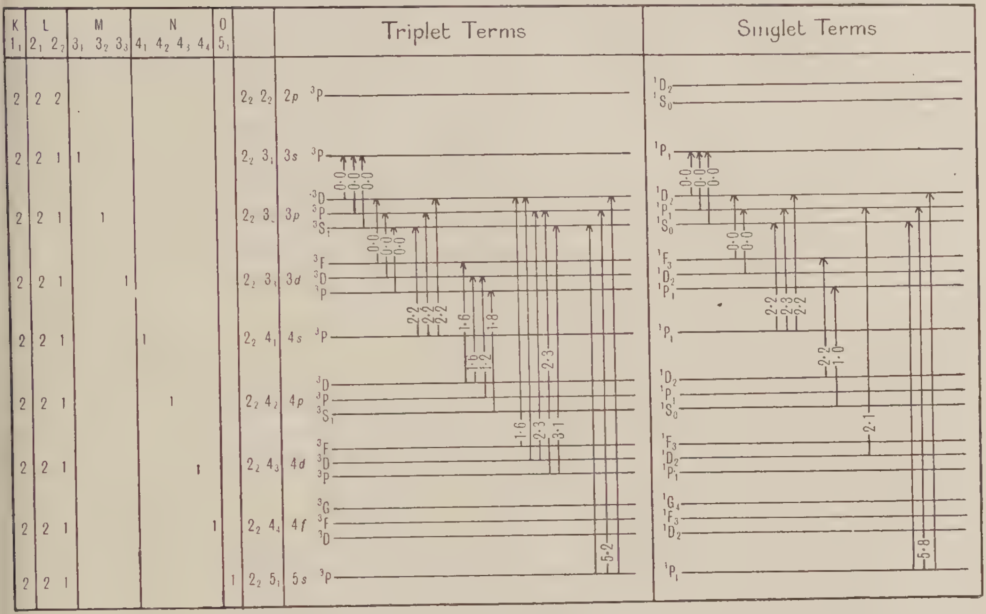
* Pressure approximately 0·7 cm.

† Pressure approximately 2·0 cm., the spark gap being slightly different from (i).

Table 2 gives the shifts corresponding to the different terms. For some of the lines in the spectrum measurements have been made at two different pressures. The corresponding term shifts are included in Table 2, and it will be seen that the ratios of the shifts at the two pressures are practically equal, the shift increasing as the pressure increases.

The terms of N II predicted by the theory of Heisenberg and Hund are shown in Table 3. Transitions giving rise to unsteady lines are shown by means of arrows, broken in order to insert the term shift. For completeness the transitions between terms arising from the 3_1 orbit and the 3_2 orbit have been included in the scheme, and their stability is indicated by attributing to them zero shift. It is to be borne in mind that these numbers do not represent any absolute property of the terms, but indicate the relative effect on the different terms. For by increasing the pressure

Table 3. Transitions and corresponding shifts



K	L		M			N				O			Triplet Terms	Singlet Terms
1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1				
2	2	2									$2_2\ 2_2$	2*p*	^3P	$^1D_2$ $^1S_0$
2	2	1	1								$2_2\ 3_1$	3*s*	^3P	$^1P_1$
2	2	1		1							$2_2\ 3_2$	3*p*	^3D ^3P $^3S_1$	$^1D_2$ $^1P_1$ $^1S_0$
2	2	1			1						$2_2\ 3_3$	3*d*	^3F ^3D ^3P	$^1F_3$ $^1D_2$ $^1P_1$
2	2	1				1					$2_2\ 4_1$	4*s*	^3P	$^1P_1$
2	2	1					1				$2_2\ 4_2$	4*p*	^3D ^3P $^3S_1$	$^1D_2$ $^1P_1$ $^1S_0$
2	2	1						1			$2_2\ 4_3$	4*d*	^3F ^3D ^3P	$^1F_3$ $^1D_2$ $^1P_1$
2	2	1							1		$2_2\ 4_4$	4*f*	^3G ^3F ^3D	$^1G_4$ $^1F_3$ $^1D_2$
2	2	1								1	$2_2\ 5_1$	5*s*	^3P	$^1P_1$

in the discharge tube, leaving the primary electrical conditions unchanged, a particular term shift is altered but, as shown in Table 2, the other terms are likewise affected. The question of the dependence of the shift on the pressure will be considered more fully later.

§ 5. RELATION BETWEEN TERMS AND TERM SHIFTS

A study of the relationships between shifts in various orbits is limited in the case of N II by the fact that no sequence of terms has been found which possesses more than three members. The first member is unaffected by the increase in pressure and therefore only two term shifts have been found for any Rydberg sequence. The results for these, however, do show that the shifts for terms arising from $n = 5$ are definitely greater than those for which $n = 4$, and as those for which $n = 3$ are zero a progressive increase of shift for increasing values of n is indicated.

Terms have been found arising from $n = 4$, $k = 1, 2, 3$, k being the azimuthal quantum number. The shifts corresponding to these terms have been obtained, but their dependence on the value of k is not evident. $4s\,^3P$ combines with $3p\,^3D$, $3p\,^3P$ and $3p\,^3S_1$, and in each case the shift is 2·2 cm.$^{-1}$, see Table 3. This in itself lends support to the assumption that the terms arising from $n = 3$ are steady or equally affected. The corresponding singlet terms behave in a similar way, the shifts being practically the same as for the triplets. For $k = 2$ the values of the term shifts are all lower than for $k = 1$, with the exception of the singlet term $4p\,^1D_2$. $4p\,^3D$ combines with $3d\,^3F$ and $3d\,^3D$ and in each combination shows the same shift. The other transitions associated with this orbit show different shifts, those for the triplet terms being greater than that for the singlet. For $k = 3$ the term shifts are practically equal to those for $k = 1$, the exception being $4d\,{}^3F$. A peculiarity arises in connection with $4d\,{}^3P$. This term combines with $3p\,{}^3P$ and $3p\,{}^3S_1$, but the groups of lines resulting from these combinations show different shifts. This would be explained if the deeper terms were unequally affected. But when the deeper terms are in combination with $3s\,{}^3P$ neither shows any shift, and in combination with $4s\,{}^3P$ the shifts are the same. Measurements on these groups showing unequal shifts were rather difficult, but the difference is thought to be real and not due to errors of measurement. At two different pressures, Table 2, the values obtained for the shifts were quite different for each combination.

§ 6. APPLICATION TO THE IDENTIFICATION OF TERMS

Although no very definite regularities have been found in the term shifts, the following rough generalisations may be made with respect to the triplet terms: (i) groups associated with n for the upper term $\leqslant 3$ are steady; (ii) shift increases as n increases; (iii) terms arising from 4_1 and 4_3 orbits show a greater effect than those from 4_2 orbits.

These rules can now be applied to the remaining lines which have not as yet been classified, and may indicate the orbits concerned in the production of the lines. For instance, within the range considered, all the multiplets that shift have already been classified with the exception of the multiplet marked *A*. That is to say, if any of the remaining lines form multiplets they are probably associated with orbits for which $n \leqslant 3$. Most of these lines have recently been classified by L. J. Freeman* and are found to belong to the quintet system. For the terms concerned in their production in no case is n greater than 3 for a steady group. The quintet system differs from the singlet and triplet systems in that the core has 2 electrons in 1_1 orbits, 1 in a 2_1 orbit, and 2 in 2_2 orbits. The series electron assumes successively the orbits 2_2, 3_1, 3_2, etc. It is interesting to note that the change in the state of the core does not affect the stability of the orbits for which $n \leqslant 3$.

As has already been mentioned, there are a few singlets which shift and as yet are unclassified. λ 6630·5 (ν 15077·7) from its wave number suggests that it belongs either to a $3_3 \rightarrow 3_2$ transition or to a $4_2 \rightarrow 3_3$ transition. As it shifts, the latter alternative is definitely indicated. If we assume that it corresponds to $3d\,{}^1P_1 - 4p\,{}^1S_0$†, the value for $4p\,{}^1S_0$ is 36676·8. $4p\,{}^1S_0$ should combine with $3s\,{}^1P_1$, giving a line at ν 52981·1, and as there is a line at ν 52981·5 the assignment is corroborated. This term should also combine with $3s\,{}^3P_1$, yielding a line at ν 53228·9. There is a line at ν 53231·1, giving additional confirmation for the value 36676·8. Assuming λ 6242·5 (ν 16014·75) to be $3d\,{}^1F_3 - 4p\,{}^1D_2$, we obtain a value of 36153·27 for $4p\,{}^1D_2$. This term in combination with $3s\,{}^1P_1$ should give a line at ν 53504·7 which is probably represented by the line at ν 53500·8.

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* The author is indebted to Mr L. J. Freeman for access to results prior to publication.

† $3d\,{}^1P_1 = 51754{\cdot}5$. Value taken from paper by Fowler and Freeman, whence

$$4p\,{}^1S_0 = 51754{\cdot}5 - 15077{\cdot}7 = 36676{\cdot}8.$$

Another suggested singlet is λ 2799·20 (ν 35714·0) as $3p\,^1P_1$–$4d\,^1D_2$, giving $4d\,^1D_2 = 28919{\cdot}8$, which should combine with $3p\,^1D_2$, yielding a line at ν 45315·3. Actually there is a fairly strong line at ν 45314·7, superposed on $3p\,^3S_1$–$5s\,^3P_0$, which suggests that the term has been correctly identified.

A fairly strong line at λ 1991·0 (ν 50216) shows a large shift of the same order as the group at λ 2290. It seemed probable therefore that the upper term would arise from an orbit for which $n \geqslant 5$. Trial showed it to be

$$3p\,^1D_2 - 5s\,^1P_1 \quad (74235{\cdot}1 - 24018{\cdot}7 = 50216{\cdot}4).$$

The results obtained are collected in Table 4.

Table 4

	$4p\,^1D_2$* 36153·27
$3s\,^1P_1$ = 89657·96	53500·8 (1)
$3d\,^1F_3$ = 52168·02	16014·75 (5)
	$4p\,^1S_0$* 36676·8
$3s\,^1P_1$ = 89657·96	52981·5 (4)
$3s\,^3P_1$ = 89905·7	53231·1 (2)
$3d\,^1P_1$ = 51754·5	15077·7 (2)
	$4d\,^1D_2$* 28919·78
$3p\,^1P_1$ = 64633·77	35713·99 (4)
$3p\,^1D_2$ = 74235·10	45314·7 (3)

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* Newly identified terms. Other term values are taken from the paper of Fowler and Freeman.

It seems likely therefore that the method might be useful as a supplement to the main methods of spectrum analysis; firstly by indicating which groups belong to the deeper and which to the higher terms, and secondly by assisting particularly in the identification of singlets, which are usually more difficult to classify than multiplets owing to the absence of characteristic wave-number separations.

§ 7. NATURE AND CAUSE OF SHIFT

Shifts in spectral lines as obtained in an ordinary discharge tube can usually be attributed to one or more of the following causes: (i) Doppler effect; (ii) pressure effect; (iii) current density effect; (iv) Stark effect.

In the present case the lines are broadened and displaced towards the red and the intensity distribution in the shifted line, as far as could be ascertained visually, is symmetrical about the middle of the line. There is no broadening in the direction of decreasing wave length. The shift from the undisturbed position is therefore approximately one-half the width of the shifted line. In the Doppler effect the whole spectrum would be affected, the shift being a function of the wave length. With the excitation employed in the present experiments the effect would probably be to produce an asymmetrical broadening which would be reversed on changing the direction of the discharge. No such effect was observed, and the conclusion is drawn that the shift is not due to the Doppler effect.

A question next arises as to the possibility of the observed shifts being due to a pure pressure effect, analogous to that observed in arc spectra. In order to find out how far pressure was responsible for the effect, the following observations were made:

(i) The primary current through the induction coil, the capacity and the pressure being kept constant, photographs were taken with the series gap at 3 mm., 4 mm. and 5 mm. The shifts increased with the increasing spark gap, as will be seen from Table 5. It will be noticed that the ratios of the shifts for the two different spark gaps are approximately the same for each group. This showed quite definitely that pressure could not be wholly responsible for the shift.

Table 5. Variation of shift with series gap

Pressure 2·5 cm.				Pressure 1·1 cm.			
Group	Gap = 3 mm. Å.U.	Gap = 5 mm. Å.U.	Ratio 5 mm./3 mm.	Group	Gap = 4 mm. Å.U.	Gap = 5 mm. Å.U.	Ratio 5 mm./4 mm.
λ 3600 (triplet)	·40	·76	1·9	λ 3600	·29	·44	1·5
λ 3007 (singlet)	·30	·67	2·2	λ 3007	·18	·29	1·6
				λ 3800 (triplet)	·33	·52	1·5

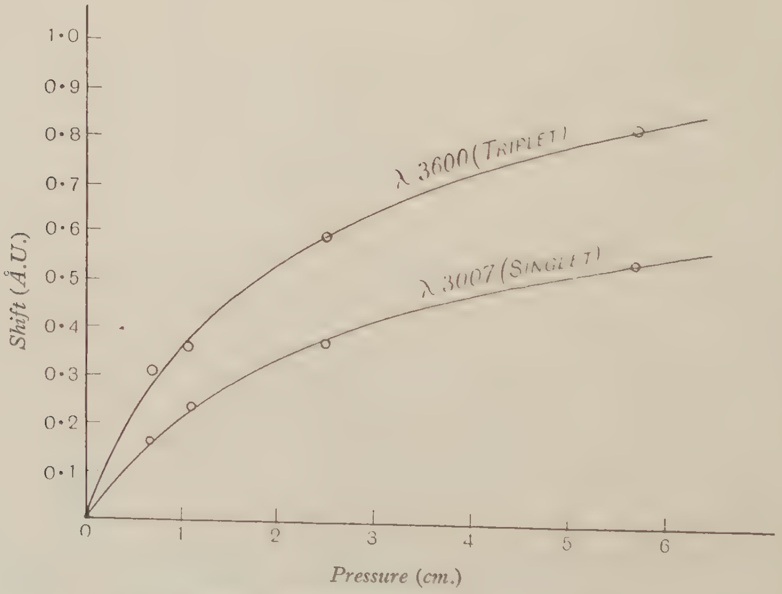

Fig. 1. Relation between shift and pressure (capillary tube).

(ii) The spectrum was obtained from the discharge through nitrogen in a tube of about 4 mm. bore, the electrodes being about 10 cm. apart. For the same pressure the shift under these conditions was much less than in the capillary tube, indicating again that the shift was not entirely due to the pressure.

(iii) With the same tube as in (ii) but with the electrodes only 1 cm. apart a spark was passed in nitrogen at atmospheric pressure, and in this case also the shift was less than in the capillary when the pressure there was 5 cm.

(iv) In the photographs taken with the discharge through a capillary tube it was observed that the lines emitted by the tail-piece of the discharge (*i.e.* the region between the electrode and the entrance to the capillary) showed less shift than those emitted in the capillary. This indicated that in the same tube at the same pressure the shift depended on the region of the discharge in which the line was emitted.

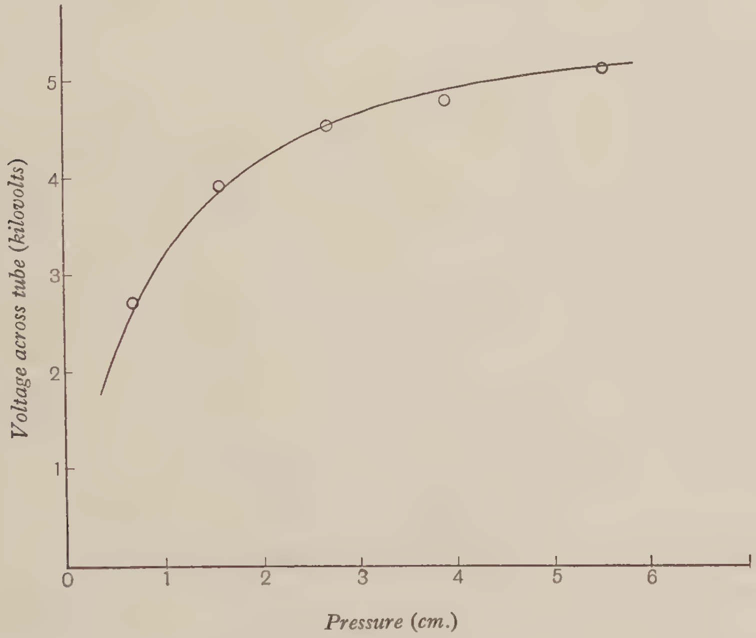

Fig. 2. Relation between voltage across tube and pressure.

(v) The primary current, series gap and capacity being kept constant, photographs were taken at several pressures up to about 5 cm., the discharge tube being of the capillary type. Beyond 5 cm. the lines became too broad and diffuse for measurement. The results are shown graphically in Fig. 1. It is seen that the rate of increase of shift with pressure in the tube is large at first and then gradually diminishes, tending to become quite small and fairly constant.

Experiments were continued with the tube running as in (v), the object being to determine how the electrical conditions varied as the pressure increased. A hot-wire ammeter was included in the secondary circuit but it was found that as measured in this way the current was approximately constant over the range of pressures employed. This result was due to the integrating effect of the ammeter, which measured only the root-mean-square current; this was approximately constant in virtue of the fact that the primary current was kept constant.

It was decided therefore that the voltage across the discharge tube should be investigated by means of an auxiliary spark-gap. In this way a fairly good value of the peak voltage can be obtained and its variation with the pressure in the tube can be determined quite readily. Fig. 2 shows the graph obtained by plotting voltage against pressure. It bears an obvious resemblance to that in Fig. 1. From these two curves the pressure was eliminated by the derivation of a third curve showing variation of shift with voltage across the tube (Fig. 3).

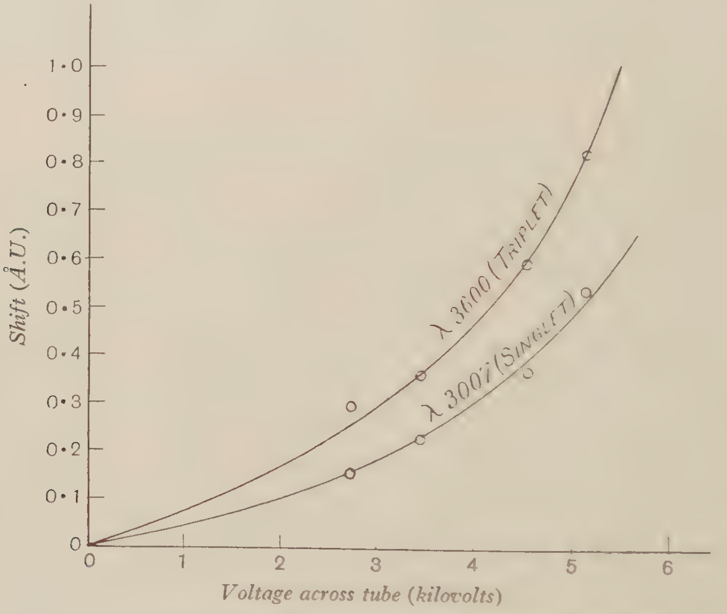

Fig. 3. Showing relation between shift and voltage across tube.

The results of observations made in (i), (ii), (iii) and (iv) showed beyond doubt that the shift was not due merely to an increase in pressure. This conclusion suggested that the change in electrical conditions brought about by a change in pressure was in the main responsible for the effect. The results of observations made in (v) supported this view and in fact seemed to indicate that the shift is in the nature of a Stark effect. In this connection it is interesting to compare the results obtained above with those obtained by Liebert* on the Stark effect for the principal series of helium (orthohelium). He found that the lines show a displacement to the red and are unresolved, the shift increasing with *n* as in the present case. The variation of shift with voltage for helium was as shown in Fig. 4. The similarity between these curves and those for N II (Fig. 3) is most marked, and points once more to the probability that the "pressure effect" in N II is mainly a Stark effect.

* *Ann. d. Phys.* **56**, 593 (1918).

On the assumption that this is the case, it is of interest to note the different conditions under which the two effects are observed. For observations of the Stark effect the gas is usually kept at a very low pressure, and it is in the region near the cathode that the effect manifests itself. In the present case the shift increases with the pressure, and observations are made with the pressure at about 1–5 cm.; further, the shift is observed throughout the capillary. The difference in the conditions is more apparent than real, for in the normal case the discharge is uncondensed, and at very low pressures by far the greater part of the potential drop is across the cathode dark space and makes this region particularly suitable for observation of the Stark effect. The spectrum of N II is produced by condensing the discharge and this makes the electric intensity along the tube much more uniform, and in the H-type tube used in the present experiments it is actually greater in the capillary than at the electrodes, as shown by observations on lines emitted by the capillary and tail-piece. So that, although the conditions are different, the determining factor in each case is the electric intensity.

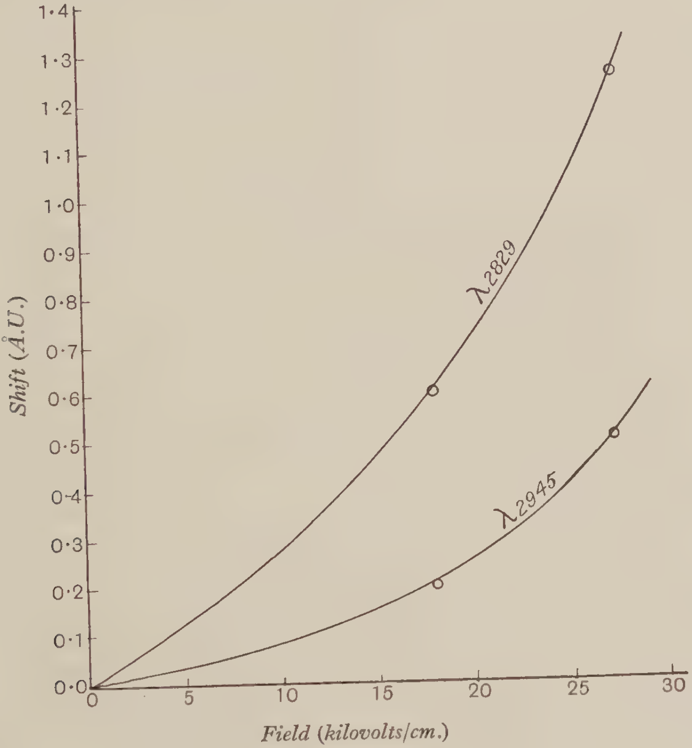

Fig. 4. Liebert's results for helium.

A word of explanation should perhaps be added in regard to the curves. In Figs. 1 and 3 they have been drawn through the origin, although no observations were made at pressures less than 0·7 cm. Fig. 2, showing the relation between voltage and pressure, has not been continued to the origin because at very low pressures the voltage actually becomes very large owing to the high resistance of the rarefied gas. The passage of curves in Figs. 1 and 2 through the origin must be regarded as an extrapolation of the results at higher pressures and not as showing, necessarily, the true state of affairs in the immediate neighbourhood of the origin.

§ 8. COMPARISON WITH THE PRESSURE EFFECT IN ARC SPECTRA

Investigations of the pressure effect have been confined chiefly to the examination of arc, spark and furnace spectra at pressures of 1 atmosphere and upwards. Much of the earlier work suffered in definiteness from the inherent difficulty of measuring lines emitted under high pressures. St John and Babcock* showed that the pole effect may seriously interfere with observations on the pressure effect.

Quite recently the pressure effect for many lines of the Fe arc spectrum has been made the subject of a very careful investigation by Babcock† who took special precautions to eliminate pole effect. The range of pressure was from a vacuum to 1 atmosphere, the errors involved in measuring the shifted lines being thus reduced. The results, in so far as they have a corresponding feature in the present case, may be summarised as follows: (i) Depression of the spectral terms with increase of pressure, the depression being greater for terms of high level than for those of low level and greater for terms of high multiplicity than for those of low multiplicity at the same level; (ii) proportionality between change of pressure and displacement of lines. Babcock also discusses the results of Gale and Adams‡ for titanium and shows that they exhibit the same features.

These results are very similar to those obtained for N II, the chief difference being in the magnitudes of the shifts in the two cases. For whereas in the present case a change in pressure from 0 to 5 cm. produced a shift of the order of 1 wave number, the shift in the Fe lines when the pressure was changed from vacuum to 1 atmosphere was only of the order of 10^{-2} wave number. It has been shown above that the effect in the case of N II is closely allied to a Stark effect and is really not a direct result of pressure. One is naturally led to consider whether this correspondence exists in the case of arc spectra, and, if it does, how much of the pressure effect is due to a Stark effect.

The relation between the pressure effect and the Stark effect is perhaps best considered through the medium of the pole effect. Takaminé§ has shown that there is an exact qualitative agreement between the pole effect and the Stark effect for several lines of the Fe arc spectrum. Quantitatively the agreement is approximately correct. Babcock‖ compared his results for the pressure effect with the observed pole effect for many Fe lines. He found that although there is an apparent connection for lines of group *d*¶ the relation disappears for lines of groups *a* and *b* and

* *Astrophysical Journal*, **42**, 1 (1915).

† *Astrophysical Journal*, **67**, 240 (1928).

‡ *Astrophysical Journal*, **35**, 10 (1912).

§ *Astrophysical Journal*, **50**, 23 (1919).

‖ *Loc. cit.*

¶ Pressure group classification *a*, *b*, *c*, *d* of Gale and Adams, *Astrophysical Journal*, **35**, 10 (1912). A further group *e* has been added by St John and Miss Ware, *Astrophysical Journal*, **38**, 209 (1913). Group *c* has recently been eliminated, *Trans. Int. Astr. Union*, **3**, 30 (1929).

in the case of lines of group *e* the shifts are in opposite directions in the two effects. This evidence, Babcock observes, draws a clear distinction between the pole effect and the pressure effect. Assuming then that the pole effect is really a Stark effect, it follows that the pressure effect for the Fe arc spectrum is not a Stark effect. The counterpart in arc spectra to the effect observed in N II appears to be the pole effect rather than the pressure effect.

It has been seen that for N II the shift due to pressure, as such, must be very small compared with the shift due to change in the electrical conditions, but the observations made in the present investigation have not yielded any precise information on this point.

Shifts of lines in the spectra of N III and argon have been found during the present work and these are being investigated together with those in O II and O III.

§ 9. ACKNOWLEDGMENT

The author wishes to express his thanks to Prof. A. Fowler for suggesting the investigation and for his invaluable advice and criticism during its progress.

THERMAL DIFFUSION AT LOW TEMPERATURES

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ABSTRACT. Measurements of thermal diffusion were made with one side of the apparatus at about 15° C. and with the other at temperatures down to about – 190° C. For mixtures such as H_2-CO_2, H_2-N_2O, H_2-C_2H_4, where one constituent easily liquefies, the separation is proportional to $\log (T_1\ T_2)$ throughout the whole range investigated, where T_1 is the absolute temperature of the hot side and T_2 that of the cold side. For mixtures such as H_2-N_2, H_2-CO, H_2-A, which can be examined at lower temperatures, the separation is at first proportional to $\log (T_1\ T_2)$, and then falls below the proportional value. In mixtures of N_2-A this falling off at low temperatures is more pronounced. From these measurements values of k_t, the ratio of the coefficient of thermal diffusion to the coefficient of ordinary diffusion, can be obtained over a considerable range of temperature. It is suggested that the behaviour at low temperatures may be explained by the fact that real molecules cannot be regarded as point centres of repulsive force only. The general behaviour of a mixture of H_2-O_2 is similar to that of H_2-N_2 or H_2-A. It is found that thermal diffusion is unaffected by reduction of the pressure to about one-fourth of an atmosphere. This result is in agreement with theoretical prediction.

§1. INTRODUCTION

PROF. S. CHAPMAN has shown theoretically how the thermal diffusion* effect in a mixture of two gases depends upon the temperature gradient applied. If λ_1 and λ_2 are the proportions by volume of the heavier and lighter gases respectively, so that $\lambda_1 + \lambda_2 = 1$, and a temperature gradient is applied in the direction x, we shall have in the steady state which is reached

$$\frac{d\lambda_1}{dx} = -\frac{d\lambda_2}{dx} = -k_t . \frac{d(\log T)}{dx},$$

where T is the absolute temperature. k_t, as defined in the theory, is the ratio of the coefficient of thermal diffusion to the coefficient of ordinary diffusion. It determines the amount of separation in any given case. Over a distance within which k_t may be regarded as constant, the resulting separation will be proportional to log (T_1/T_2), T_1 being the temperature of the hot side and T_2 of the cold side. The value of k_t depends upon the masses and sizes of the molecules, and upon the proportions of the two gases in the mixture; it also depends upon the nature of the forces operating during collision, being a maximum for rigid elastic spheres, while it disappears entirely for molecules obeying an inverse fifth power law of repulsion.

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* D. Enskog, *Phys. Zeit.* **12**, 538 (1911); *Ann. d. Phys.* **38**, 742 (1912). S. Chapman, *Proc. Roy. Soc.* A, **93**, 1 (1916); *Phil. Trans.* A, **217**, 157 (1917); *Phil. Mag.* **34**, 146 (1917); **38**, 182 (1919); **48**, 602 (1924); *Proc. Roy. Soc.* A, **119**, 34 (1928); **119**, 55 (1928); *Phil. Mag.* **7**, 1 (1929). Chapman and Dootson, *Phil. Mag.* **33**, 268 (1917). T. L. Ibbs, with a note by S. Chapman, *Proc. Roy. Soc.* A, **99**, 385 (1921); **107**, 470 (1925). Ibbs and Underwood, *Proc. Phys. Soc.* **39**, 227 (1927). Elliott and Masson, *Proc. Roy. Soc.* A, **108**, 378 (1925).

In practice it is convenient to make measurements on thermal diffusion by observing the difference in composition in two vessels maintained at steady temperatures and joined by a connecting tube. The difference in percentage composition by volume of the gas in two such vessels will be termed the percentage separation. In a series of experiments* made with a number of mixtures of different gases, one vessel being at a steady temperature of about 15° C. and the other at temperatures up to about 300° C., it was found that for any given mixture the percentage separation was closely proportional to $\log(T_1/T_2)$, so that over this range k_t could be regarded as constant. (Elliott and Masson†, with a hot side at about 500° C., obtained relatively greater separation for a number of gas mixtures). Any deviation from this proportionality was not greater than the possible error of the experiments. Thus for this range of temperatures the behaviour of the gases could be represented by molecules which are point centres of force obeying a constant inverse-power law of repulsion, although it is possible that the same behaviour might be represented by a more complicated molecular model.

At the time of publication of the results of an earlier series of experiments, Prof. Chapman suggested to one of us (T. L. I.) that it would be interesting to make experiments with one vessel at the temperature of liquid air. A preliminary experiment, made with the object of testing this suggestion for a mixture of hydrogen and nitrogen, showed that the amount of separation was relatively less than that obtained in experiments at higher temperatures. This apparent change in the value of k_t suggested the need for a more complete investigation to discover, if possible, the nature of the change and to find if it occurred in other gas mixtures also.

When experiments are made over an extended range of temperature, the separation produced by thermal diffusion may be considerable. The resulting variation in the proportions of the gases in different parts of the connecting tube will itself produce some variation in the value of k_t, and the possible effect of this fact must be considered when the results are examined.

§ 2. METHOD OF EXPERIMENT

In this work we have attempted to make a general study of the phenomenon at low temperatures rather than a close examination of any special pairs of gases. When the work was begun there was little to indicate which would be the most profitable gases to study. For the present purpose we simplified the experimental work by keeping as closely as possible to our original methods, and using considerable quantities of gas. Further experiments are now in progress dealing with gases in smaller quantities; this work requires more manipulation, and progress is consequently slower.

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* T. L. Ibbs, *loc. cit.* (1925).

† *Loc. cit.*

We examined each gas mixture by keeping one side of the apparatus at practically constant temperature by means of a flow of water from the mains, and making measurements with the other side at a number of temperatures down to that of liquid air, or down to the point where one of the constituents liquefied. The principle of the experiment was similar to that previously adopted, with one large and one small vessel joined by a connecting tube. With this arrangement practically the whole effect of thermal diffusion can be made to appear as a change in composition of the gas in the smaller vessel. A diagram of the apparatus is shown in Fig. 1. The katharometer* was again used, but it was convenient in this

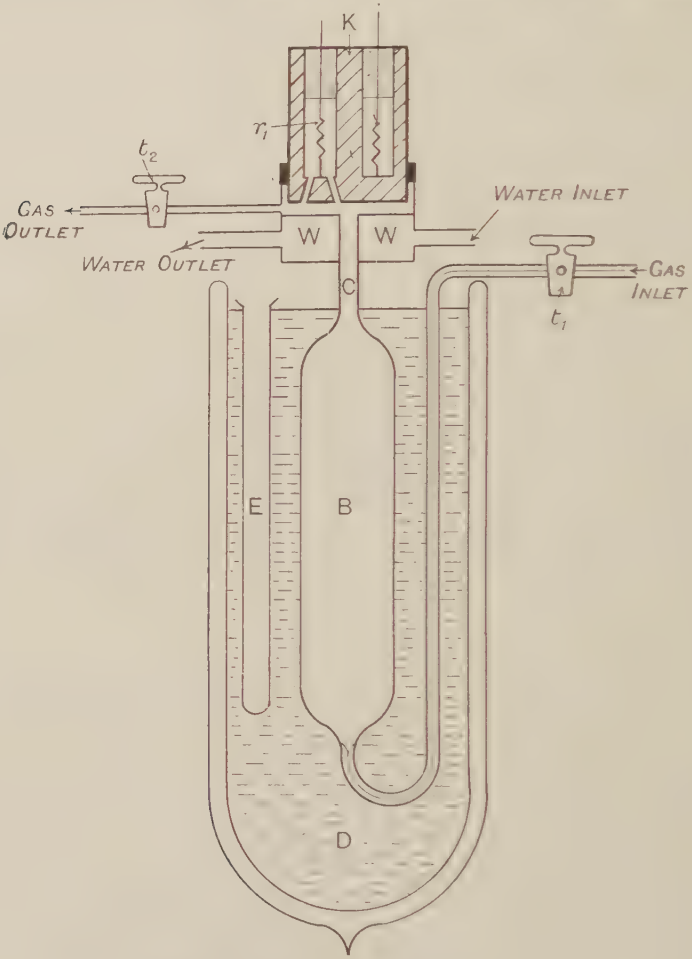

Fig. 1. Diagram of apparatus.

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* This instrument was kindly lent by Dr G. A. Shakespear.

case to put the katharometer block K at the top; this block is kept at constant temperature by means of the water jacket W. The exposed cell r and its connections, with a total volume of 1·0 c.c., form what must now be regarded as the small hot side, all at the temperature of the water jacket. The hot side is joined by means of a connecting tube C of length about 3 cm. and internal diameter 0·4 cm. to the glass bulb B, of volume 45·0 c.c., which forms the large cold side. The bulb B was cooled by means of a surrounding Dewar vessel D, generally containing a cooling liquid such as liquid air or cold pentane. This arrangement of the apparatus, with the cold side below, avoids errors which might arise owing to convection and also enables the cooling liquid to be applied without difficulty. By a rapid flow of water maintained through W the katharometer was effectively screened from the cooling effect of the liquid in the Dewar vessel.

The gas mixture to be examined was made in a cylinder under pressure, and sufficient time was allowed for it to attain uniformity of composition. The Dewar vessel containing a cooling liquid was put in position, and the apparatus was flushed out, the gas mixture entering at tap t_1, passing through the glass capillary tube to the cold bulb B, through the connecting tube C, past the katharometer block, and out at the tap t_2. The method was again adopted of allowing the gas to pass sufficiently quickly through the connecting tube to overcome the effect of thermal diffusion, so that the whole apparatus was filled initially with a mixture of uniform composition. The flow was then stopped, the taps were closed, and the resulting change in composition on the hot side was measured by means of the katharometer. The corresponding change in composition of the gas in the glass bulb of the cold side can be calculated; this change depends upon the relative volumes of the hot and cold sides, and upon their temperatures. With the present arrangement the change on the cold side is small, being only about 0·006 of the change on the hot side, when the bulb B is in liquid air.

The electrical arrangements of the katharometer were similar to those previously employed, and the general use of the instrument was the same as before.

Method of cooling. Many preliminary experiments were made in order to develop a suitable method of cooling the glass bulb to a number of temperatures, down to that of liquid air. In the early experiments freezing mixtures were used, such as ice and sodium chloride. Carbon dioxide snow was also used either alone or mixed with methylated spirits. Although these methods presented practical difficulties in obtaining uniform temperatures, the thermal diffusion effect was clearly shown. A typical set of results for a mixture of hydrogen and nitrogen is given in Fig. 2. It will be seen that the separation is proportional to $\log(T_1/T_2)$ down to the point given by carbon dioxide snow, and that if the straight line is produced, the point corresponding to the separation and temperature produced by liquid air lies considerably below it. This fact indicated the need for using a number of temperatures below that of carbon dioxide snow, more especially as few ordinary gases can be taken to the liquid air temperature without liquefaction occurring. Pentane was finally adopted as the cooling liquid. This was generally cooled in the Dewar vessel before it was placed round the bulb B. A large test-tube was placed in the pentane, and liquid air poured into it, causing the pentane to cool rapidly. The Dewar vessel was then placed round the bulb. For the lower temperatures it was necessary to cool the pentane further, when the Dewar vessel was in position. In this case a small tube E was put into the pentane (Fig. 1), and a quantity of liquid air injected into it, so as to cause a further fall in temperature of the bulb B. (The liquid air required for this purpose was kept in a second Dewar vessel, fitted with a cork, mouthpiece, and delivery tube, and it was blown over as required into the tube E.) In this way the temperature of the bulb could be controlled to some extent, and a mixture of gases could be cooled until one constituent liquefied. This method of controlling low temperatures is somewhat similar to that described by Patterson*.

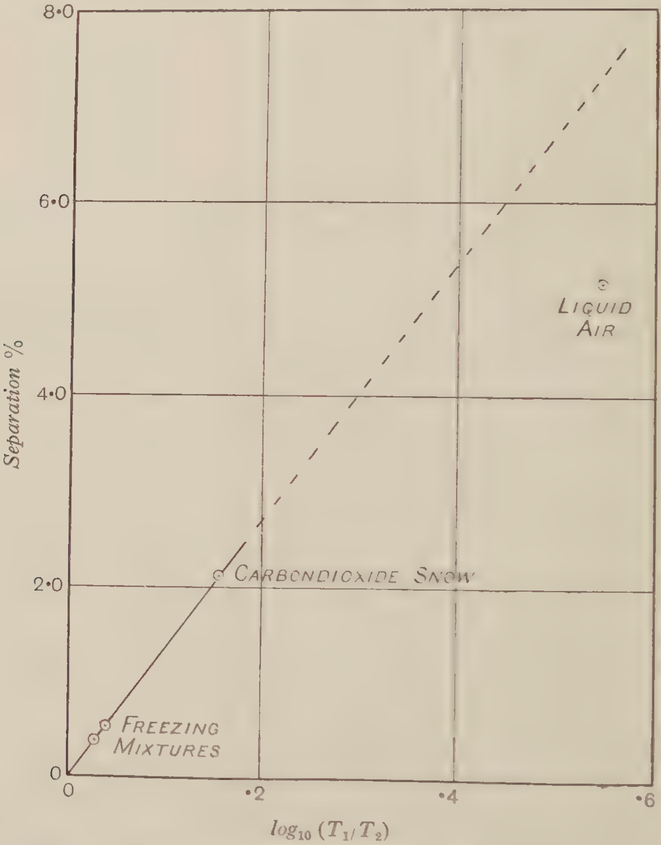

Fig. 2. Preliminary experiments (35·8 % H_2, 64·2 % N_2).

It was necessary to stir the pentane to keep the whole of the bulb B at practically the same temperature. Several different methods of stirring were tried, and the method finally adopted was to bubble compressed air from a cylinder through the liquid. This was found to be more effective than the use of a mechanical stirrer, and it did not cause any serious rise in temperature of the contents of the Dewar vessel. At – 125° C. the rise in temperature was about half a degree per minute, which did not produce any difficulty in making the observations. Using the method described, we were able to obtain temperatures down to about – 140° C.; as the pentane solidified at about – 150° C.

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* W. H. Patterson, *Phil. Mag.* **2**, 383 (1926).

As we experienced difficulty in obtaining supplies of pentane of lower freezing point, it was necessary to devise a method of obtaining temperatures between – 140° C. and – 190° C. The use of a liquid as a cooling medium had to be abandoned, and the following method was substituted. The same Dewar vessel was used, and a quantity of cotton wool was placed at the bottom. A piece of thin copper sheet was bent into the form of a tube lining the inner walls of the vessel, and resting on the cotton wool. The vessel was filled with liquid air and then emptied, except for the small quantity remaining absorbed in the cotton wool. It was then placed in position round the bulb B, which had previously been immersed for a short time in liquid air, and the mouth of the Dewar vessel was plugged tightly with cotton wool. In this way we found that a minimum temperature, of about – 170° C. at the middle of the bulb, could be obtained. This would remain steady for 15 minutes or longer, depending on the quantity of liquid air in the wool. The temperature then began to rise, slowly at first, and then more rapidly. Thermal diffusion measurements were made during the steady period, and the initial parts of the rise. As heat enters the vessel from its mouth, it was not possible in the use of this method to avoid a fairly uniform temperature gradient throughout the length of the bulb. With the middle of the bulb at – 170° C. there was a temperature difference of about 20° between its ends: this temperature gradient will produce some thermal diffusion in the bulb itself. Simple considerations of the thermal diffusion effect show that with the present arrangement of a small hot side and a large cold side, we introduce little error by regarding the temperature at the middle as the temperature of the bulb, and measuring the change in composition on the hot side as before. Measurements made in this way at rather higher temperatures were found to be in satisfactory agreement with those obtained by the use of pentane, and the portion of the curves obtained by this method terminated smoothly in the point obtained by the use of liquid air.

In mixtures containing hydrogen the thermal separation was practically complete in about five minutes, but it was observed that the rate at which the effect took place tended to be less at the lower temperatures.

The temperature measurements. The cold side temperatures were measured down to – 120° C. with a toluol thermometer graduated in degrees. For lower temperatures a pentane thermometer, also marked in degrees, was used. The thermometers were normally supported in the Dewar vessel with the bulb near the middle of the glass bulb B. A constant volume hydrogen thermometer was made and was used to check the accuracy of the thermometer readings. The toluol thermometer was found to be correct to within a degree over its entire range. The error of the pentane thermometer was greater and was variable, but not sufficiently to have any serious effect on our results. The simplicity gained by the use of this thermometer was an important point in its favour.

The temperature of liquid air was measured by the hydrogen thermometer and was found to be – 192° C. after the liquid air had been standing for two or three hours; it was convenient to adopt this in a number of cases as the liquid air temperature.

A thermo-couple was used for some of the temperature measurements; it was calibrated by means of the hydrogen thermometer.

The hot side temperature was measured by means of an ordinary mercury thermometer placed in the water, where it issued from the water jacket.

Miscellaneous details. The measurements were generally made at atmospheric pressure. Pressures can therefore be regarded as atmospheric, unless otherwise shown. The process of flushing out with the gas was repeated for each measurement.

The gases used were taken from cylinders. To prevent errors due to the condensation of water vapour or other easily liquefied impurities, the gas mixtures were passed through a U-tube immersed in liquid air or cooled pentane, before entering the apparatus. In this way such impurities could be removed. Small amounts of other impurities would have no serious effect on the results.

Most of the mixtures now used had previously been examined at higher temperatures, and it was convenient to use the old katharometer calibration curves which had been obtained on another instrument. This procedure will not affect the general nature of the results, and it should not cause any serious error in the absolute amounts of separation now recorded. The initial portions of the curves given by these low-temperature experiments yield values of k_t which are in reasonable agreement with values obtained from our previous higher-temperature experiments. This is evidence for the consistency of the method of measurement. Minor differences occasionally occur: for example, the values of k_t for mixtures of hydrogen and nitrous oxide are lower than previously recorded. There is little doubt that in due course we shall be able to adjust any such irregularities.

§ 3. EXPERIMENTAL RESULTS

Eight pairs of gases were examined. It is convenient to divide the experiments into three groups for the consideration of results.

Group 1. Measurements on mixtures of (*a*) hydrogen and carbon dioxide; (*b*) hydrogen and nitrous oxide; (*c*) hydrogen and ethylene.

Group 2. Measurements on mixtures of (*a*) hydrogen and nitrogen; (*b*) hydrogen and carbon monoxide; (*c*) hydrogen and oxygen; (*d*) hydrogen and argon.

Group 3. Measurements on mixtures of nitrogen and argon.

Each pair of gases was examined in mixtures of three or more different proportions. Each mixture was examined with the cold side at about eight different temperatures, ranging from about – 30° C. to – 192° C., or to the liquefaction point of one of the constituents if this was above – 192° C. In a series of measurements on a given mixture, the temperature T_1 of the hot side rarely varied by more than 1° C., so that the values of $\log (T_1/T_2)$ can be regarded as referring to definite hot and cold side temperatures. For different mixtures, the hot side temperature may differ rather more widely, as shown in the tables.

As the primary object of these experiments is to investigate the variation of thermal separation with temperature, curves have been plotted showing the relation between separations as ordinates and $\log_{10}(T_1/T_2)$ as abscissae. The value of k_t determines the slope of these curves since, over a given distance dx,

$$k_t = -\,d\lambda_1/d\,(\log T).$$

With the present arrangement, where the hot side temperature can be regarded as constant for any given mixture, the slope of the curve at any point is proportional to the value of k_t in a region where the temperature is T_2, i.e. the cold side temperature corresponding to the point. Hence numerical values of k_t can be obtained, if required, from the slope of the curves.

It will be found that the first portion of the curve is in all cases a straight line, so that k_t can be regarded as constant over a considerable temperature range. The changes in slope which occur in many cases at the lower temperatures indicate a gradual fall in the value of k_t as T_2 is reduced. In no case does the value of k_t appear to increase as the temperature is lowered.

The differences in slope of the curves shown for different mixtures of any given pair (see, for example, Fig. 3) are due, of course, to the different proportions of the two gases in the mixtures. This dependence of k_t on the proportions of the gases in the mixture has already been investigated experimentally, and the results are in agreement with the theoretical prediction.

With our present arrangement of a small hot and a large cold side, the separating effect of thermal diffusion will cause the proportion of the lighter gas to increase, from the cold end to the hot end of the connecting tube. Most of the mixtures we have now examined have been arranged to contain less than 50 per cent. of the lighter gas, which was generally hydrogen: this means that the separating effect in the connecting tube will on the whole tend to cause a small apparent increase in the value of k_t as T_2 is reduced. The change is small, but it appeared desirable to make it opposite in sign to the interesting falling off in the value of k_t which we have observed at lower temperatures.

Group 1. *Hydrogen and* (*a*) *carbon dioxide;* (*b*) *nitrous oxide;* (*c*) *ethylene.* For all these pairs, one of the constituents liquefies at a temperature above that of liquid air. Measurements could be made in these cases down to within about 1° of the liquefaction point by cooling the pentane when in position round the bulb, as described. If liquefaction occurred in the cold bulb, it was immediately indicated by the katharometer's showing a sudden increase in the proportion of hydrogen.

Fig. 3 shows the results for three mixtures of hydrogen and carbon dioxide. It will be seen that the separation is closely proportional to $\log(T_1/T_2)$ even when the liquefaction point of the carbon dioxide is approached. This proportionality at the low temperatures is striking, and means that k_t is constant over this range of temperature. If there were any serious change from the ordinary gas conditions at the lower temperatures, we should expect some deviation to be shown.

Clustering of the molecules would probably affect the thermal diffusion and thus produce a change in the value of k_t, or it would produce a partial separation in the mixture, with a consequent alteration in the proportions on the two sides, quite apart from the effect of thermal diffusion. All these mixtures behaved in the same way. The constant value of k_t in these cases, as the liquefaction point is approached, is of special interest when we come to consider the results of other mixtures.

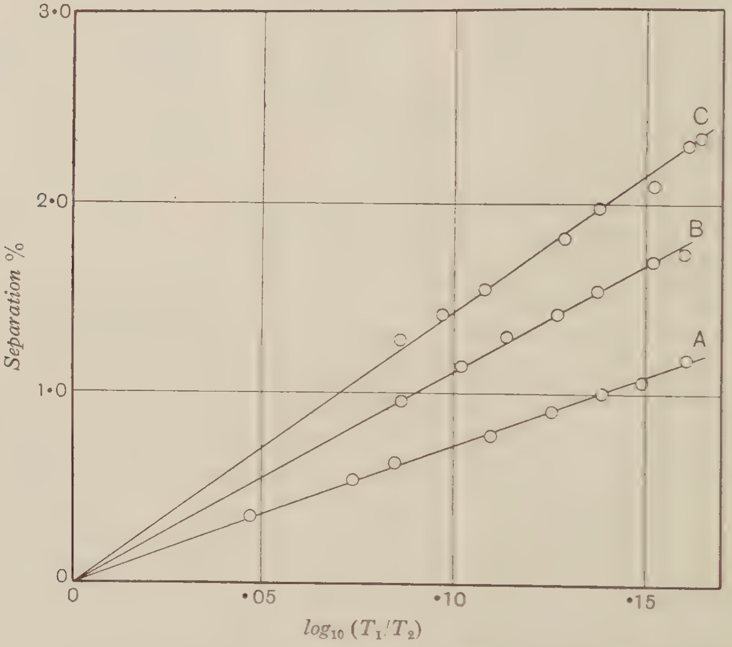

Fig. 3. H_2-CO_2 mixtures. *A*, 18·4 % H_2; *B*, 34·0 % H_2; *C*, 45·2 % H_2.

The results for hydrogen and nitrous oxide are similar to those for hydrogen and carbon dioxide and are shown in Table 5. The liquefaction point of ethylene (− 102° C.) is somewhat lower than that of carbon dioxide, but proportionality is still observed. Measurements were made at temperatures down to − 98° C. (see Fig. 4).

Group 2. (*a*) *Hydrogen and nitrogen*. Low temperature measurements on mixtures of this pair can be made over a wide range, the cold side being taken down to the temperature of liquid air, i.e. to within a few degrees of the liquefaction point of nitrogen. Preliminary experiments on this pair had already shown that the separation produced when the cold side is at liquid-air temperature is proportionally less than the normal amount. By means of the methods described, complete curves could now be obtained down to the liquid-air point, as shown in Fig. 5 for two mixtures. They show that the separation is proportional to log (T_1/T_2) until the cold side reaches about − 100° C. At lower temperatures the proportionality no longer holds, the separation falling below its ordinary value, until at − 190° C., the total separation is about 20 per cent. less than normal. This falling off in the effect begins at temperatures which can be attained by the method of cooling with pentane. The amount by which the observed separation falls below the normal value is approximately the same for all the mixtures, as is also the temperature at which the departure from the normal value begins.

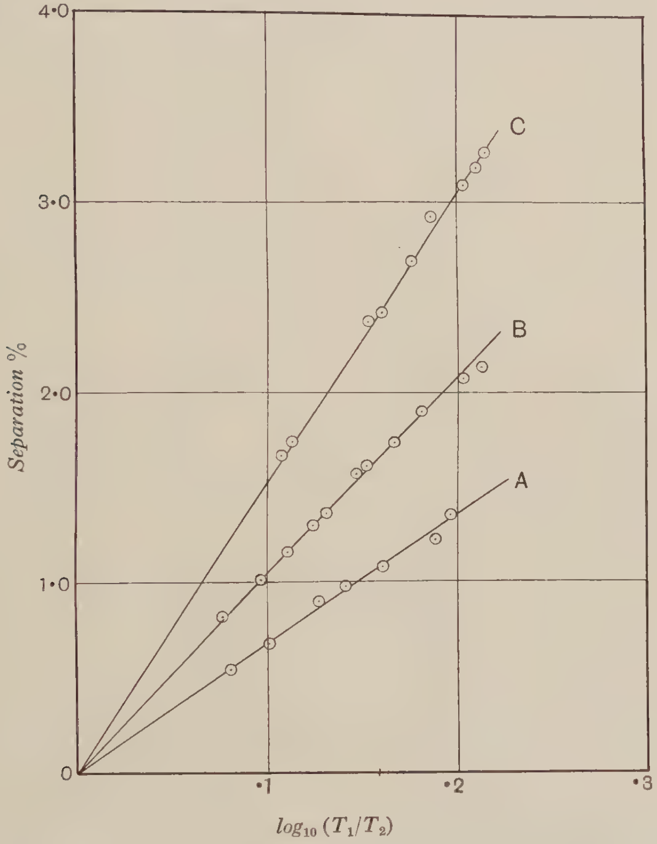

Fig. 4. Mixtures of H_2-C_2H_4. *A*, 16·5 % H_2; *B*, 28·0 % H_2; *C*, 58·5 % H_2.

Group 2. (*b*) *Hydrogen and carbon monoxide*. The low liquefaction point of carbon monoxide makes it a suitable gas for low-temperature investigation. It is of interest also to compare the behaviour of mixtures of this pair of gases, with that of mixtures of hydrogen and nitrogen. We again find that the behaviour of the two pairs is similar. Below about − 100° C. the separation is no longer proportional to log (T_1/T_2). At − 192° C. the observed value is again about 20 per cent. below the normal or proportional value. The results are shown in Table 8.

Group 2. (*c*) *Hydrogen and oxygen*. These are the first measurements which we have made on this pair of gases. The mixture which was examined showed the falling off in the effect at low temperatures; the behaviour of oxygen with hydrogen being very similar to that of nitrogen with hydrogen. The results are shown in Table 10.

Group 2. (*d*) *Hydrogen and argon*. The preceding experiments have shown that for mixtures of certain diatomic gases with hydrogen, the proportionality between the separation and log (T_1/T_2) does not hold at low temperatures. In the present case argon is substituted for the diatomic gas. Argon was chosen because it is available in sufficient quantities for this method of experiment and has a suitably low liquefaction point, – 186° C., although measurements cannot be made at atmospheric pressure with the use of liquid air. The curves obtained are similar to those given by the previous mixtures in this group, see Fig. 6. At – 170° C. the observed separation is about 16 per cent. below the proportional value. The cold side temperature at which the proportionality begins to fail is about – 80° C., and it thus appears to be definitely higher than in the cases already considered.

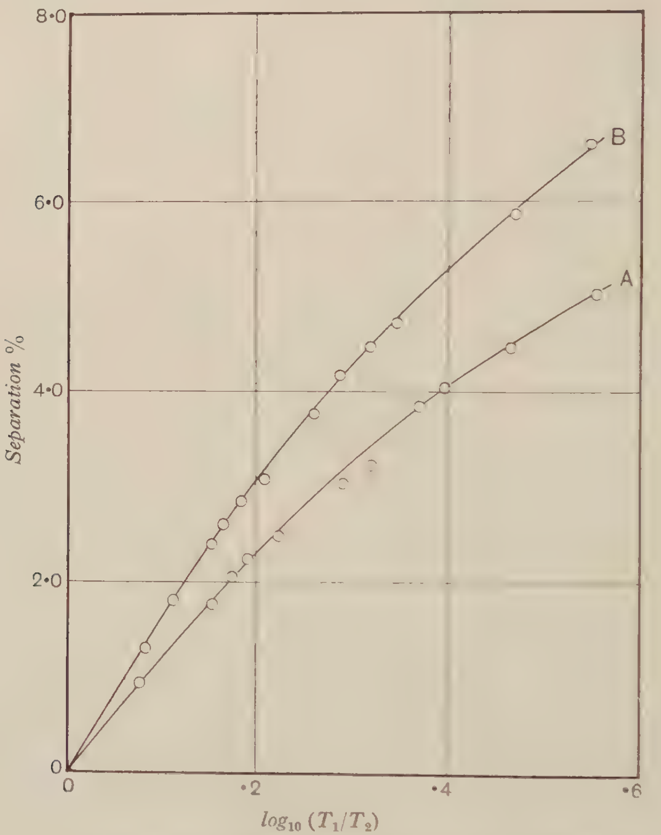

Fig. 5. Mixtures of H_2-N_2. *A*, 29·4 % H_2; *B*, 42·0 % H_2.

Group 3. *Nitrogen and argon*. All mixtures previously examined in this work have contained hydrogen, so that measurements could be taken down to the liquefaction point of the other constituent. The lightness of the hydrogen molecule also enables a considerable separation to be obtained and so assists the accuracy of the measurements.

However unlikely it may appear, there was a possibility that the falling off in the value of k_t at low temperatures might have been due to some unique property of hydrogen. It was desirable therefore to find a pair of gases, not containing hydrogen, which could be examined at low temperatures. Nitrogen and argon mixtures were suited to our purpose, as both gases are available in suitable quantities. Three different mixtures were examined.

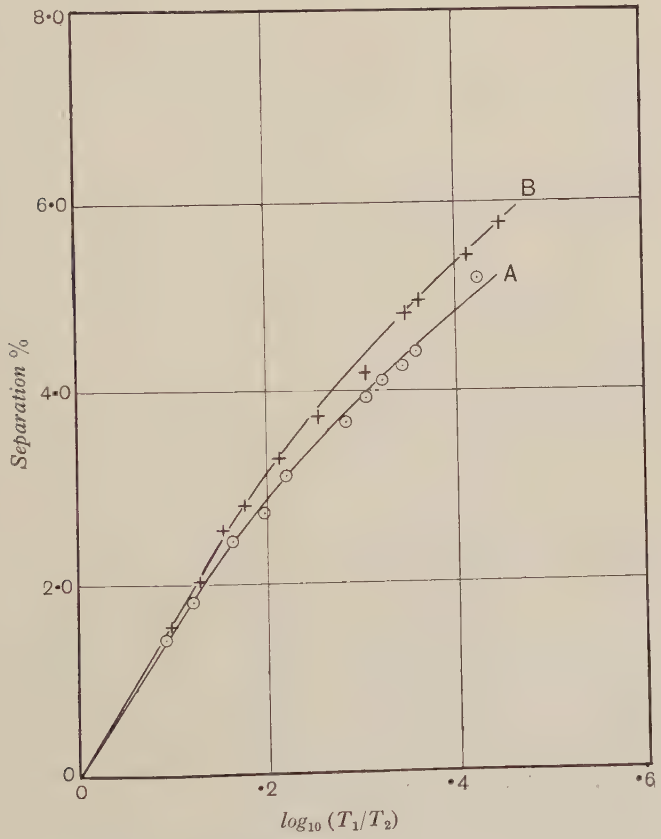

Fig. 6. Mixtures of H_2-A. *A*, 47·0 % H_2; *B*, 55·6 % H_2.

The actual amount of separation was less than before, because the masses of the molecules are more alike. The measurements cannot therefore be made with the same degree of accuracy. The time taken to reach the steady state was much longer than for hydrogen mixtures.

The results for two mixtures are shown in Fig. 7. It will be seen from the curves that the falling off in the value of k_t is much more pronounced than in any previous case. The observed separation at − 170° C. is about 40 per cent. below the ordinary proportional value, or about twice the reduction shown in the hydrogen mixtures of Group 2. This fact suggests that the deviation may be due not to the hydrogen molecules, but rather to the nitrogen, argon or other molecules in the mixtures.

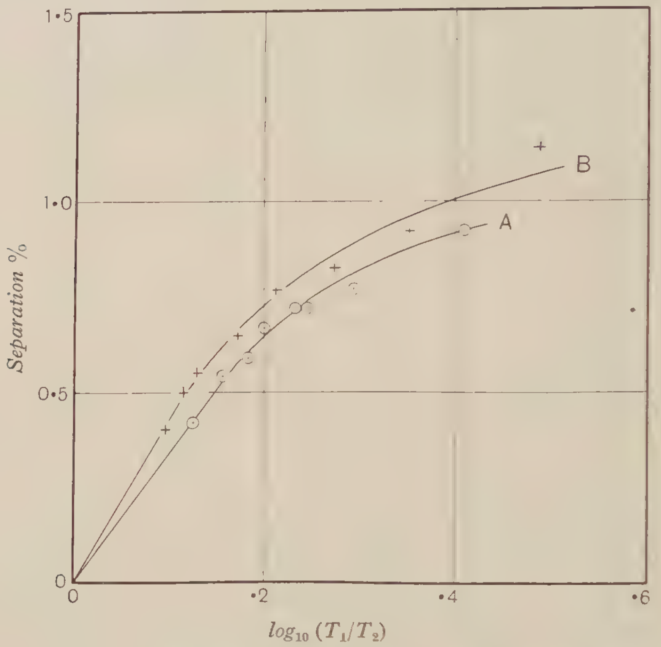

Fig. 7. Mixtures of N_2-A. *A*, 70·0 % N_2; *B*, 46·0 % N_2.

§ 4. MEASUREMENTS OF THERMAL DIFFUSION MADE UNDER VARYING GAS PRESSURES

The question arises, whether the nature of our results at the low temperatures is due to a departure from the simple gas conditions postulated in the theory. Experiments made on the variation of the viscosity of gases with temperature show that the behaviour is not normal at the lower temperatures. Thus, a number of observers* have shown that the observed values of the coefficient of viscosity at low temperatures is greater than that predicted by Sutherland's law. Various attempts have been made to explain this effect as due to clustering of the molecules, multiple encounters or other causes. Reference will be made later to the work of Lennard-Jones, who regards the ordinary gas conditions as still holding.

In our case, the measurements of Group 1 have already suggested that the gas conditions which are generally postulated in the kinetic theory can be regarded as holding until one of the constituents liquefies. This suggests that the behaviour of the mixtures in Groups 2 and 3 is not due to a departure from the simple gas conditions, although the temperatures used are now lower. A further test of the persistence of the simple gas conditions may be applied by means of measurements of thermal diffusion made under different gas pressures. By reducing the pressure, we may expect to reduce the possibility of molecular aggregation or multiple encounters.

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* For references see S. Chapman, *Phil. Trans.* A, **216**, 342 (1916).

For these experiments the flow method, which had previously been used, was discontinued. The apparatus was first filled with a mixture at atmospheric pressure, the large glass bulb *B* being at the temperature of the room, and both taps closed. The cooling liquid was then placed round the glass bulb, causing thermal diffusion to take place, and also reducing the pressure of the gas inside the apparatus. The extent to which the pressure was reduced depended of course upon the temperature of the cooling liquid. When liquid air was used the pressure inside the apparatus was reduced to about 0·27 of the initial pressure.

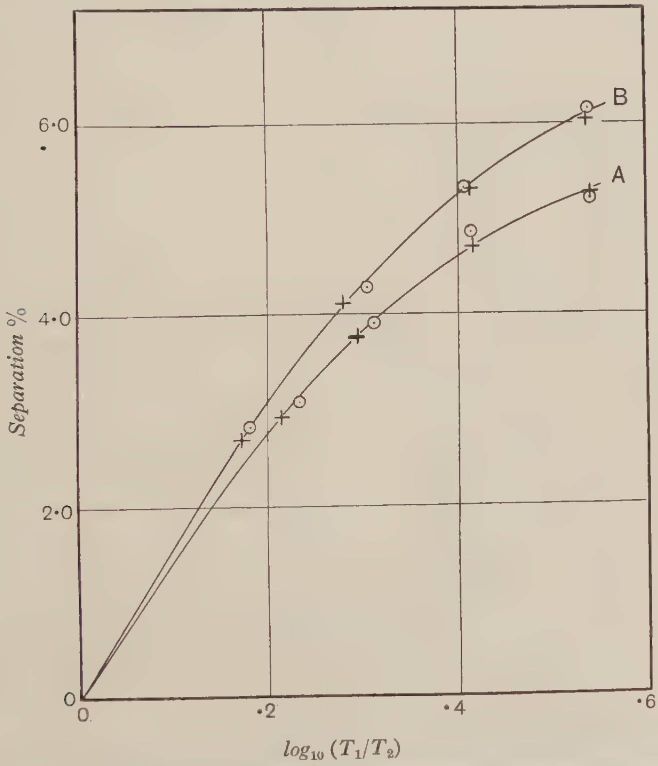

Fig. 8. Experiments with varying pressure. +, atmospheric pressure; ⊙, reduced pressure; *A*, 36·0 % H_2, 64·0 % CO; *B*, 43·5 % H_2, 56·5 % N_2.

The reduction of pressure inside the apparatus will itself affect the katharometer readings, the change in readings for any given pressure depending upon the gas mixture used. The necessary correction for this effect can be made by means of a separate experiment, in which the apparatus is first filled with the gas mixture at atmospheric pressure. The pressure is then reduced by means of a pump, and the effect of the change in pressure on the readings of the galvanometer is directly observed. In this way a curve can be plotted for any given mixture, showing the effect of change of pressure on the readings, and by reference to this curve the necessary correction can easily be made.

Thermal diffusion measurements were thus made under reduced pressure on mixtures of hydrogen and nitrogen and of hydrogen and carbon monoxide. Measurements were also made on the same mixtures in the usual way at atmospheric pressure. In this way it was found that the two sets of measurements gave practically identical results. In Fig. 8 it will be seen that the falling off in the effect at low temperatures is the same for both methods of measurement. This fact appears to afford satisfactory evidence of the simplicity of the gas conditions. The evidence is supported by the work of Dewar* who concludes "that either a simple or compound gas, at an initial pressure somewhat less than one atmosphere, may be relied on to determine temperatures down to its own boiling point, in the constant volume gas thermometer." We are therefore justified in not attributing the peculiarities of thermal diffusion at low temperatures to a failure in the gas conditions.

Apart from their value for this special purpose, the results of these experiments made under varying pressures supply additional confirmation of the general theory. All our measurements have previously been made at atmospheric pressure. The theory shows that the effect depends upon the proportions of the gases in a mixture, and not upon the molecular density of the constituents. The value of k_t will therefore be independent of the pressure of the gas. This prediction is now confirmed experimentally. A more detailed study of thermal diffusion over an extended range of pressures would be interesting.

§ 5. DISCUSSION OF RESULTS

Experiments on the variation of viscosity with temperature have shown that, over a limited range of temperature, the molecules of gases can be represented as point centres of repulsive force obeying an inverse power law†. This discovery provided the first information on the nature of inter-molecular forces in gases. The behaviour of viscosity over an extended range of temperature cannot generally be explained by means of molecules of this type, and Sutherland's model, which allows for the attractive forces between molecules, in some cases gives better agreement. In thermal diffusion we are dealing with the forces between molecules of different kinds, but the behaviour in collisions will probably be of a similar general character to that in collisions between the molecules of a simple gas.

The constant value of k_t which we have observed over a limited range of temperature for all pairs of gases suggests that the molecules might again be regarded as point centres of repulsive force. The falling off in the value of k_t at the lower temperatures might be due to a change in the nature of the collisions as the temperature is reduced. If we regard molecules simply as point centres of repulsive force, then we must consider them to become softer as the temperature falls, i.e.

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* Dewar, *Proc. Roy. Soc.* **68**, 49 (1901).

† Cf. Jeans, *Dynamical Theory of Gases*, 3rd edition, para. 380.

the index of the power law is reduced. A better representation of real molecules appears to be given by regarding them as point centres of both attractive and repulsive force. This model has been used very successfully by Lennard-Jones* in a number of cases. For example, a close representation of the viscosity of argon can be obtained over the entire range of temperature for which it has been observed. The theory of thermal diffusion, which at present deals with molecules as point centres of repulsion only, is highly complex. Chapman has shown that there is little prospect of developing a simple physical theory like those applied to many of the phenomena considered by the kinetic theory, and any attempt to extend the theory to include the effects of attractive forces will no doubt further increase its complexity. The general nature of our experimental results suggests, however, that the decrease in the value of k_t at the lower temperatures may be due to the effect of these attractive forces. As the temperature is reduced the molecules penetrate less deeply into the fields of force during an encounter. The attractive forces of the van der Waals' type become relatively more important than the repulsive forces with increasing distance; and it seems possible that the effect of this circumstance on the nature of the collisions may be equivalent to a softening of the molecules at the lower temperatures. Definite conclusions on this question can only be reached with the aid of a complete theoretical investigation. It appears unlikely that the observed behaviour of thermal diffusion at low temperatures can be due directly to the effective change in the sizes of the molecules.

The range of temperature in which the gases of Group 1 can be examined does not extend below about − 100° C., and the value of k_t is practically constant in that group. This does not necessarily mean that repulsive forces only are operating during an encounter. The superposed attractive and repulsive fields may produce the effect of a repulsive field, with power law of lower index. More exact experiments may show that there is a definite variation in k_t over this range, but it is probable that any such variation will be very small.

For Group 2 k_t can again be regarded as constant over a considerable range, after which it decreases with temperature. It is interesting to compare the experimental value of k_t obtained at different temperatures for a mixture of hydrogen and nitrogen with the theoretical value for rigid elastic spheres. Using Chapman's formulae† with numerical values inserted for hydrogen-nitrogen mixtures, we obtain

$$k_t = \frac{5}{2}\left[\frac{0{\cdot}220\lambda_1 + 0{\cdot}195\lambda_2}{1{\cdot}784 + 1{\cdot}430\,\lambda_1/\lambda_2 + 0{\cdot}438\,\lambda_2/\lambda_1}\right].$$

Applying this, we find that $k_t = 0{\cdot}0984$ for rigid elastic spheres, corresponding to a mixture containing 29·4 per cent. of hydrogen. From the slope of the curve shown in Fig. 5 we obtain the experimental values of k_t for different temperatures of the cold side T_2. These values are shown in Table 1.

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* Lennard-Jones, *Proc. Roy. Soc.* A, **106**, 441 (1924); **107**, 157, 636 (1925); **109**, 584 (1925); **112**, 214 (1926); **115**, 334 (1927).

† *Phil. Mag.* **48**, 602 (1924).

Table 1

T_2	0° C.	− 50° C.	− 100° C.	− 150° C.	− 190° C.
k_t experimental	0·050	0·050	0·043	0·032	0·025
$\dfrac{k_t \text{ experimental}}{k_t \text{ rigid elastic spheres}}$	0·51	0·51	0·435	0·315	0·255

Thus the experimental value of k_t at − 190° C. is about half the value obtained at ordinary temperatures. Other curves for mixtures of these gases yield similar results. The curves for other gas mixtures can be dealt with in the same way.

The measurements on mixtures of hydrogen and oxygen are the first which we have made on this pair of gases. It is interesting to observe that the general behaviour of the pair, which combine chemically, is similar to that of hydrogen and argon. Thus chemical affinity does not appear to have any direct bearing on the thermal diffusion effect, and this fact suggests that such affinity does not influence the nature of the forces arising between molecules during collisions. The similarity mentioned above applies to the general amount of separation, and to the falling off at lower temperatures. Experiments made by Masson and Dolley* on the compressibilities of mixtures of ethylene and oxygen, and of ethylene and argon, showed that the behaviour of the two mixtures was practically the same. They therefore conclude that the van der Waals' attraction between the molecules of different gases in a mixture does not arise from chemical affinity. Our observations showing that chemical affinity does not appear to have any direct influence on the thermal diffusion effect afford general support to such a conclusion. Chemical forces and cohesive forces may both be of electronic origin, but there is probably a fundamental difference in their nature. We hope in due course to make further experiments dealing with this aspect of the subject.

For oxygen-hydrogen mixtures Chapman and Hainsworth give

$$k_t = \frac{5}{2}\left\{\frac{0{\cdot}204\lambda_1 + 0{\cdot}177\lambda_2}{1{\cdot}630 + 1{\cdot}320\lambda_1/\lambda_2 + 0{\cdot}405\lambda_2/\lambda_1}\right\}.$$

Applying this formula to a mixture containing 29·8 per cent. of hydrogen, we find that $k_t = 0{\cdot}100$. Comparing this with experimental values, by using a curve as before, we obtain the results shown in Table 2.

Table 2

T_2	0° C.	− 50° C.	− 100° C.	− 150° C.	− 180° C.
k_t experimental	0·048	0·048	0·043	0·024	0·020
$\dfrac{k_t \text{ experimental}}{k_t \text{ rigid elastic spheres}}$	0·48	0·48	0·43	0·24	0·20

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* Masson and Dolley, *Proc. Roy. Soc.* A, **103**, 524 (1923).

For mixtures of nitrogen and argon the variation of k_t with temperature is reater. As before, we obtain the general formula for k_t for rigid elastic spheres orresponding to nitrogen-argon mixtures. Thus

$$k_t = \frac{5}{2}\left\{\frac{0\cdot100\lambda_1 + 0\cdot116\lambda_2}{3\cdot693 + 1\cdot748\lambda_1/\lambda_2 + 1\cdot889\lambda_2/\lambda_1}\right\}.$$

Applying this to a mixture of 30 per cent. argon, we find that $k_t = 0\cdot0314$. From he slope of the curve shown in Fig. 7 we again obtain experimental values of k_t n regions corresponding to different temperatures of the cold side T_2. These values re shown in Table 3.

Table 3

T_2	0° C.	− 50° C.	− 100° C.	− 150° C.	− 180° C.
k_t experimental	0·0148	0·0148	0·0075	0·0036	0·0016
$\dfrac{k_t \text{ experimental}}{k_t \text{ rigid elastic spheres}}$	0·472	0·472	0·239	0·114	0·051

Measurements of the viscosity of hydrogen at low temperatures show that Sutherland's law is not followed. Better representation of the experimental results is given by regarding the molecules as point centres of repulsive force*. This means that for hydrogen the attractive forces are weak; thus in mixtures of nitrogen and argon we may expect the attractive forces between unlike molecules to be greater than in mixtures with hydrogen as one constituent. The great variation with temperature in the experimental value of k_t for nitrogen-argon mixtures gives support to this view.

It is interesting therefore to consider the possibility of obtaining a pair of gases for which the value of k_t will remain constant down to − 190° C., or for which its variation with temperature will be small. Lennard-Jones has shown that the attractive forces for both helium and neon are weak. We may therefore expect that in mixtures of helium and neon or hydrogen and neon the influence of the attractive forces will be small. Experiments dealing with these two pairs of gases and with other mixtures containing inert gases are now in progress. For this extension of the work considerable modification of the apparatus and method is required.

Tables showing the results of a final series of measurements have been included in the paper so that they may be available if required for the purpose of calculation.

§ 6. ACKNOWLEDGMENT

In conclusion, we desire to express our thanks to Prof. S. W. J. Smith, who has granted full facilities for this work.

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* Cf. Jeans, *Dynamical Theory of Gases*, p. 286.

Table 4. Hydrogen and carbon dioxide

18·4 % H_2 $T_1 = 11°$ C.			34·0 % H_2 $T_1 = 12°$ C.			45·2 % H_2 $T_1 = 13°$ C.		
$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %	$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %	$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %
− 76·2	·161	1·18	− 76·1	·160	1·74	− 76·4	·164	2·34
− 71·1	·149	1·06	− 72·0	·152	1·69	− 75·5	·161	2·30
− 66·9	·139	1·00	− 65·1	·137	1·53	− 71·1	·152	2·09
− 60·5	·126	0·91	− 60·0	·127	1·42	− 65·2	·138	1·97
− 52·2	·110	0·78	− 53·9	·114	1·29	− 60·5	·129	1·82
− 39·4	·085	0·63	− 47·8	·102	1·14	− 49·8	·108	1·55
− 33·6	·074	0·54	− 39·5	·087	0·96	− 43·9	·097	1·41
− 17·0	·047	0·34				− 38·0	·086	1·28

Table 5. Hydrogen and nitrous oxide

35·0 % H_2 $T_1 = 15°$ C.			42·5 % H_2 $T_1 = 13°$ C.			59·0 % H_2 $T_1 = 14°$ C.		
$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %	$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %	$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %
− 78·2	·169	1·68	− 85·5	·183	2·02	− 86·0	·186	2·31
− 66·0	·143	1·43	− 80·0	·170	1·87	− 74·3	·161	2·03
− 53·0	·117	1·18	− 74·8	·161	1·81	− 65·5	·141	1·81
− 44·5	·100	0·98	− 59·5	·126	1·49	− 53·0	·116	1·47
− 29·0	·071	0·72	− 42·9	·094	1·08	− 39·0	·089	1·13
			− 37·8	·085	0·98			
			− 30·2	·072	0·84			

Table 6. Hydrogen and ethylene

17·0 % H_2 $T_1 = 15°$ C.			28·0 % H_2 $T_1 = 14°$ C.			58·5 % H_2 $T_1 = 14°$ C.		
$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %	$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %	$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %
− 89·8	·196	1·35	− 97·5	·213	2·14	− 98·1	·215	3·27
− 85·9	·187	1·23	− 92·8	·201	2·07	− 93·2	·203	3·10
− 74·0	·160	1·08	− 84·0	·181	1·90	− 97·3	·211	3·19
− 65·3	·141	0·99	− 71·4	·152	1·61	− 81·4	·175	2·70
− 58·3	·127	0·90	− 60·2	·130	1·36	− 71·8	·153	2·38
− 44·8	·101	0·68	− 50·5	·110	1·15	− 50·8	·112	1·74
− 33·7	·080	0·54	− 31·4	·095	0·82	− 47·9	·107	1·66

Table 7. Hydrogen and nitrogen

29·4 % H_2 $T_1 = 16°$ C.			42·0 % H_2 $T_1 = 16°$ C.			77·5 % H_2 $T_1 = 15°$ C.		
$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %	$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %	$T_2°$ C.	$\log_{10}$ (T_1/T_2)	Separation %
− 192	·552	5·02	− 192	·550	6·62	− 192	·550	6·15
− 174	·465	4·47	− 176	·472	5·87	− 174	·463	5·89
− 157	·396	4·04	− 143	·348	4·74	− 159	·402	5·42
− 150	·371	3·84	− 134	·319	4·48	− 144	·349	4·79
− 135	·321	3·22	− 124	·289	4·17	− 137	·325	4·67
− 125	·291	3·05	− 114	·260	3·77	− 130	·304	4·38
− 99	·221	2·48	− 94	·208	3·06	− 121	·277	4·14
− 86	·190	2·23	− 84	·184	2·85	− 107	·240	3·77
− 80	·175	2·04	− 75	·165	2·61	− 82	·178	2·96
− 70	·154	1·79	− 70	·154	2·41	− 29	·072	1·15
− 31	·077	0·95	− 49	·112	1·82			
			− 33	·082	1·30			

Table 8. Hydrogen and carbon monoxide

24·0 % H_2 T_1 = 11° C.			32·5 % H_2 T_1 = 12·5° C.			53·0 % H_2 T_1 = 13·5° C.		
T_2° C.	$\log_{10}$ (T_1/T_2)	Separation %	T_2° C.	$\log_{10}$ (T_1/T_2)	Separation %	T_2° C.	$\log_{10}$ (T_1/T_2)	Separation %
− 192	·545	4·73	− 192	·547	6·12	− 192	·550	7·32
− 142	·334	3·14	− 170	·443	5·19	− 167	·476	6·33
− 124	·276	2·71	− 158	·394	4·80	− 145	·351	5·22
− 102	·217	2·29	− 140	·331	4·13	− 130	·303	4·55
− 90	·188	1·92	− 126	·289	3·78	− 107	·238	3·60
− 76	·157	1·62	− 117	·263	3·54	− 89	·193	3·34
− 63	·131	1·38	− 103	·226	3·08	− 93	·201	3·46
− 40	·084	0·92	− 88	·189	2·60	− 63	·134	2·29
			− 65	·138	1·94			

Table 9. Hydrogen and argon

47·0 % H_2 T_1 = 13·5° C.			55·6 % H_2 T_1 = 16·5° C.		
T_2° C.	$\log_{10}$ (T_1/T_2)	Separation %	T_2° C.	$\log_{10}$ (T_1/T_2)	Separation %
− 165	·425	5·19	− 170	·448	5·78
− 147	·358	4·40	− 161	·412	5·43
− 143	·344	4·24	− 147	·361	4·96
− 136	·321	4·09	− 143	·348	4·81
− 131	·304	3·91	− 130	·307	4·18
− 124	·283	3·67	− 112	·258	3·72
− 108	·238	3·42	− 95	·212	3·30
− 101	·220	3·11	− 80	·176	2·80
− 83	·177	2·74	− 68	·152	2·54
− 76	·162	2·43	− 57	·128	2·01
− 55	·118	1·79	− 42	·098	1·57
− 42	·091	1·40			

Table 10. Hydrogen and oxygen

29·8 % H_2 T_1 = 17° C.		
T_2° C.	$\log_{10}$ (T_1/T_2)	Separation %
− 171	·452	4·07
− 158	·400	3·74
− 139	·334	3·43
− 126	·295	3·15
− 120	·277	2·96
− 106	·239	2·62
− 95	·212	2·35
− 86	·190	2·09
− 74	·163	1·81
− 60	·133	1·45
− 50	·112	1·26
− 31	·078	0·88

Table 11. Nitrogen and argon

46·0 % N_2 T_1 = 16° C.			62·5 % N_2 T_1 = 16·5° C.			70·0 % N_2 T_1 = 17·5° C.		
T_2° C.	$\log_{10}$ (T_1/T_2)	Separation %	T_2° C.	$\log_{10}$ (T_1/T_2)	Separation %	T_2° C.	$\log_{10}$ (T_1/T_2)	Separation %
− 179	·486	1·14	− 179	·488	0·95	− 159	·407	0·92
− 145	·354	0·92	− 134	·319	0·87	− 125	·294	0·77
− 119	·274	0·83	− 92	·212	0·73	− 107	·244	0·72
− 96	·213	0·77	− 72	·159	0·59	− 104	·232	0·72
− 78	·171	0·65	− 52	·118	0·46	− 89	·199	0·67
− 58	·129	0·55				− 82	·181	0·59
− 51	·115	0·50				− 70	·156	0·54
− 41	·095	0·40				− 56	·123	0·42
						− 44	·102	0·39

EXPERIMENTS ON MAGNETOSTRICTIVE OSCILLATORS AT RADIO FREQUENCIES

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ABSTRACT. An account is given of the behaviour of two magnetostrictive oscillators 6 mm. and 4·5 mm. in length, when placed in a coil in series with the main induction coil of a simple valve-maintained oscillating circuit. The frequency characteristic of the smaller oscillator is 540 kc./sec.

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§ 1. RÉSUMÉ OF PREVIOUS WORK

In previous papers* various experiments on the maintenance of mechanical oscillations by magnetostriction have been described. These experiments extended from frequencies of 2·5 to 270 kc. sec. in the case of longitudinal oscillations of nickel rods vibrating in their lowest modes with one node at the centre. The method employed at the higher frequencies was to surround the centre of the bar with a coil wound on a glass tube in which the bar could slide easily. This coil was in series with the main induction coil of a simple valve-maintained circuit of the tuned anode type. In the lead from the grid coil to the grid a microammeter was inserted to indicate the rectified grid current; this instrument served to show the effect of the reactions of the oscillations of the bar on the valve assemblage and also enabled frequencies to be determined by means of an absorption wave-meter. The bar was magnetised before insertion in the tube; the coil surrounding it carried the plate current in a direction to assist the permanent magnetism of the bar. In the previous experiments the polarisation due to these two causes was increased by placing the tube in the hollow axis of the two bored pole pieces of an electromagnet. With bars of nickel less than 1 cm. in length the current through the electromagnet could be dispensed with, the residual magnetism being sufficient; the pole pieces and electromagnet were replaced at still higher frequencies by a small permanent magnet placed near the oscillator.

By these means the experiments with nickel rods were carried down to a length of 8 mm. and a frequency of about 300 kc. sec. Pierce† having found "nichrome" to be a good material for use in magnetostriction experiments, the next shortest bar to be tried was made of "glowray," a material having the approximate composition 65 per cent. nickel, 20 per cent. iron, 15 per cent. chromium. A turned bar of glowray 7 mm. long and 2·13 mm. in diameter was annealed at a dull red heat in lime and after remagnetisation was found on testing to give a frequency of 356 kc./sec. This oscillator was shown in operation at the Exhibition of the Physical and Optical Societies 1929 and an account of the experiment is included in Dr Ferguson's description of the Exhibits in the Research and Experimental Section in the *Journal of Scientific Instruments* for February 1929.

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* *Nature*, Dec. 13, 1927; *Electrician*, Dec. 28, 1928; Jan. 4, 1929.

† *Proc. Am. Ac. of Arts and Science*, **63**, 1–47 (1928).

§ 2. APPARATUS

An account will now be given of similar experiments with two glowray bars, one 6 mm. long, the other 4·5 mm. long.

The experiments on these two bars were carried out under very similar conditions. The apparatus is shown diagrammatically in Fig. 1. L_1 is the main induction coil. It consists of 20 turns of No. 20 D.W.S. copper wire wound close together in a single layer on a former of 9·5 cm. diameter. The grid coil L_2 was a similar coil of 100 turns of No. 26 D.W.S. on a cylinder 8 cm. in diameter. It was mounted so as to be adjustable with respect to L_1 by means of a simple geometric slide provided with a linear scale. The microammeter G of the moving coil type had a resistance of 10 ohms and was used unshunted. Its maximum deflection was obtained with 240 μA. The coil L_3 in series with L_1 carries the plate current and the oscillatory current. It has 200 turns of No. 36 enamelled copper wire, wound on a thin-walled glass tube, T, Fig. 1. The glass tube was fixed in a V groove in an ebonite block, the magnet NS being placed on the bench near it. The oscillator was in a symmetrical position with respect to the windings of L_3 and the poles of the permanent magnet.

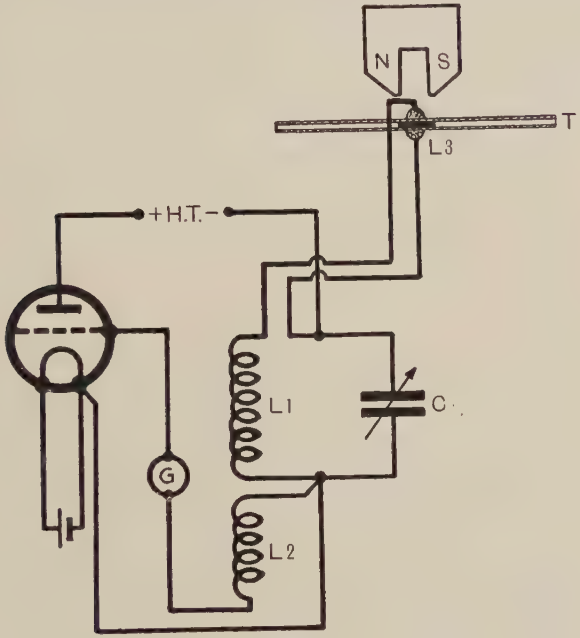

Fig. 1.

The valve was a B.T.H. G P 210 and was operated at 1·9 volts on the filament and 50 volts on the plate, with no grid bias.

§ 3. EXPERIMENTS WITH GLOWRAY OSCILLATOR 6 MM. IN LENGTH

The oscillator was 2·135 mm. in diameter. It was not found possible to detect any magnetostrictive reactions on the galvanometer until after the bar had been annealed by heating to a dull red heat in lime. The effect of the oscillations of the bar in the coil L_3 after magnetisation was then easily detected. The coupling between L_1 and L_2 was adjusted until these effects were well marked. The distance between the centres of the coils L_1 and L_2 was then about 3·5 cm. and the magnet faces N and S were about half a centimetre distant from the oscillator. Figs. 2 to 5 deal with the behaviour of this oscillator. The vertical axis on the left is graduated to indicate in the upper parts of the figures the rectified grid current in microamperes, in the lower parts the capacity of the wave-meter condenser in $\mu\mu$F, while the numbers on the horizontal scale show the value in $\mu\mu$F of the total capacity (C, Fig. 1) in the oscillatory circuit.

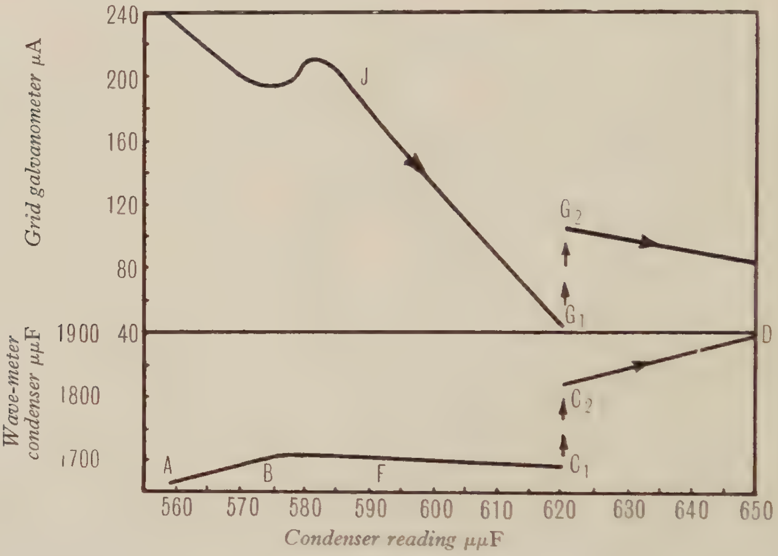

Fig. 2.

Description of Fig. 2. Starting with a small capacity C and a large grid current, the grid current falls steadily as C is increased until it reaches a minimum; the frequency which began to fall with rising capacity then becomes approximately stabilised. This is shown by the curve in the lower section of Fig. 2, the ordinates of which are the readings of the wave-meter condenser which were taken by closing the wave-meter circuit and adjusting for resonance immediately after recording the deflections of the grid galvanometer. While the value of C rises from 575 to 620 $\mu\mu$F the settings of the wave-meter condenser are almost constant, a very small change being shown over this range. If the oscillator had not been free to vibrate, the wave-meter curve would have followed a practically straight track ABC_2D, the path BC_1C_2 being replaced by the direct path BC_2.

The wave-length corresponding to 1700 $\mu\mu$F on the figure is 719 m. and the frequency 417 kc./sec.

As the capacity C is slowly increased from 575 $\mu\mu$F the grid current reaches a maximum and then steadily decreases. When the capacity in the valve set reached 620·5 $\mu\mu$F in the particular series of readings from which Fig. 2 was drawn the galvanometer deflection suddenly rose from G_1 to G_2. The value of the condenser at which this discontinuity occurred varied over a few $\mu\mu$F in different experiments. When the grid current rises from G_1 to G_2 the frequency drops from that corresponding to C_1 to that corresponding to C_2. The oscillator, although still probably executing forced vibrations, exerts little effect on the frequency of the electrical oscillations, so that the path of the wave-meter condenser readings from C_2 to D is sensibly the same as if the oscillator were clamped.

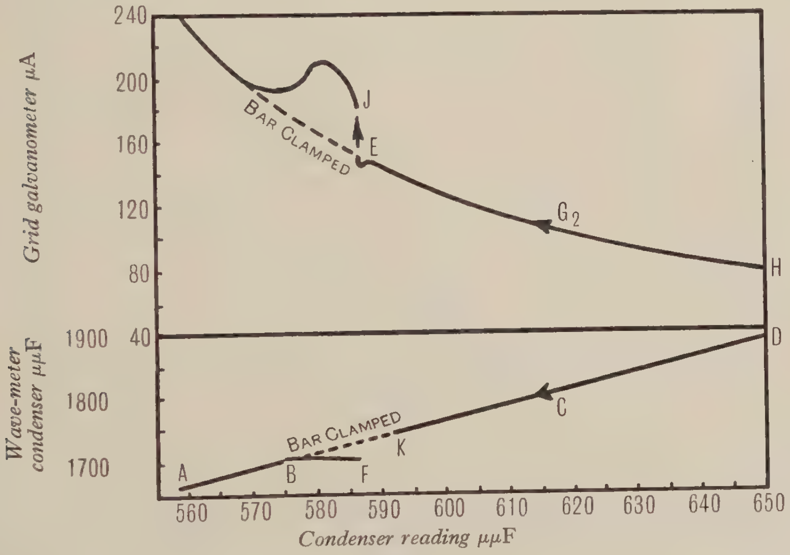

Fig. 3.

The increase in the capacity of the oscillating condenser C from 580 to the capacity at which the grid current suddenly rises is accompanied by a decrease in the wave-length and an increase in the frequency of the oscillations.

Description of Fig. 3. The values of the grid current and wave-length are not repeated as the condenser readings are traversed in the opposite direction.

Starting with a large condenser reading and a small grid current, Fig. 3 indicates the changes in grid current and wave-meter condenser as the capacity in the maintained circuit is decreased. The grid current steadily rises and the frequency increases as the capacity in the maintained set is diminished until at about 587 $\mu\mu$F the grid current drops slightly at E; on further decreasing the capacity the grid current rises slightly, but any further decrease in C now causes the galvanometer trace to increase suddenly to J, and the wave-meter condenser trace drops to the point F. The oscillating bar is now controlling the frequency. On further traversing the curves to the left the paths are sensibly the same as the corresponding portions of the curves shown in Fig. 2. If when the grid galvanometer curve had reached *E*, Fig. 3, the capacity had been again increased, the upper and lower curves would have been retraced in the direction EG_2H and *KCD*.

Description of Fig. 4. If the sudden discontinuity has occurred and the grid current has jumped to *J* and the wave-meter condenser curve to *F*, then these curves cannot be traced from left to right; that is, this discontinuity only occurs in the sense from *E* to *J* and *K* to *F*. This is illustrated in Fig. 4.

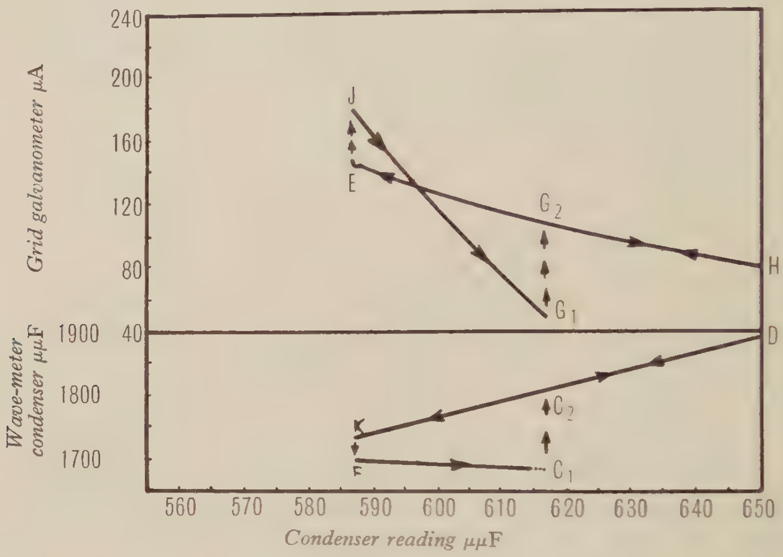

Fig. 4.

In this figure the capacity was initially 650 μμF, and is decreased until the bar takes control of the frequency when the grid galvanometer has jumped from *E* to *J*. The capacity is then increased; the curves *J* to G_1 and *F* to C_1 are traced when the discontinuity occurs in both; the bar now loses control and the galvanometer and wave-meter condenser readings rise from G_1 to G_2 and from C_1 to C_2. If *C* is still further increased, the return tracks traverse the original paths which commenced the experiment.

If, having started as in Fig. 2, we increase the capacity to a value just insufficient to cause the discontinuity in the neighbourhood of 620 μμF, we may retrace the curves in the sense *FBA* and G_1J without encountering any discontinuity.

Returning to Fig. 4, it will be seen that there are for each value of *C* between certain limits two possible frequencies and two possible grid galvanometer readings. The lines FC_1, JG_1 correspond to the stabilised state and KC_2, EG_2 to the unstabilised state.

If the filament battery is left on the valve permanently but the plate battery switched on for different values of *C*, the following results are obtained. For all values of *C* greater than that corresponding to the points *J*, *E*, *K*, *F* the galvanometer rose to the value indicated by the line EG_2H, indicating that the assemblage was oscillating in the unstabilised state. For all settings of C less than that given by J, E, K, F the galvanometer rose to points given on the curve to the left of J in Fig. 3.

For values of C corresponding closely to that given by J, E, K, F the galvanometer at first indicates an unstabilised vibration and then its pointer moves very soon afterwards to the upper stabilised position.

An example of oscillation hysteresis somewhat similar to that described above is given by Pierce* who employed a different circuit.

§ 4. EXPERIMENTS WITH DAMPED BAR

After the above experiments had been performed, powdered paraffin wax was packed into the glass tube to fill up those parts not occupied by the bar. The wax was melted by a hot wire, and after it had been cooled the results shown in Fig. 5 were obtained. The bar still showed signs of oscillating. The galvanometer and wave-meter curves were the same, no matter in which direction they were traced. The frequency indicated as stabilised when the capacity was near 582 μμF is lower than the frequency when the bar is free. The attachment of the wax thus increases the inertia more than the restoring forces of the bar. This experiment was reproduceable provided the temperature of the laboratory was low. A comparatively slight rise of temperature (three or four degrees Fahrenheit) sufficed to obliterate the effects altogether. The two curves of Fig. 5 then became quite regular, showing that when the wax was softened its viscosity prevented the bar from oscillating appreciably. The resulting curves have been drawn in as broken lines on Fig. 3, and the parts which do not lie on the previously drawn curves marked "bar clamped."

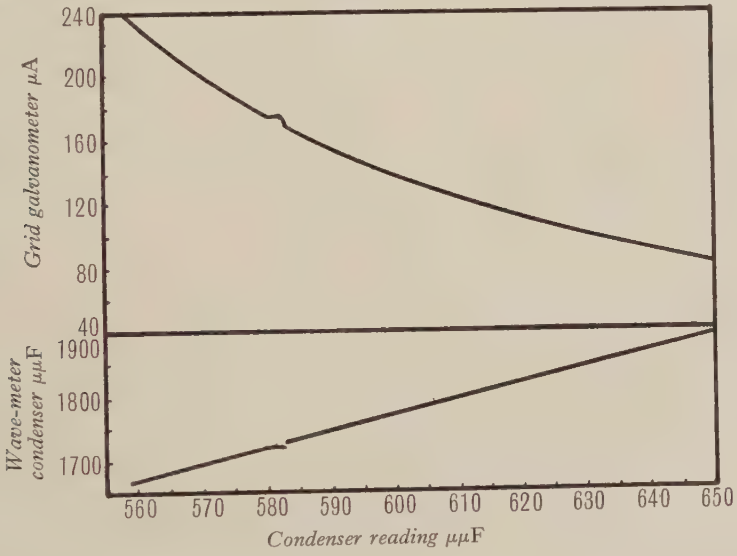

Fig. 5.

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* *Loc. cit.*

§ 5. EXPERIMENTS WITH GLOWRAY OSCILLATOR 4·5 MM. IN LENGTH

This oscillator was 2·178 mm. in diameter. After being annealed and magnetised it was placed in the same tube and surrounded by the same coil that was used for the experiments with the 6 mm. bar. There was no difficulty in finding evidence of the reaction of the bar on the oscillating set when the capacity was decreased. The grid current after decreasing rose suddenly when the capacity was so large that the bar could no longer control the frequency. On reversal of the capacity changes no evidence of reaction was at first evident, but by altering the distance of the polarising magnet and adjusting the position of the grid coil the sudden change in the conditions governing the oscillations was shown also in this direction.

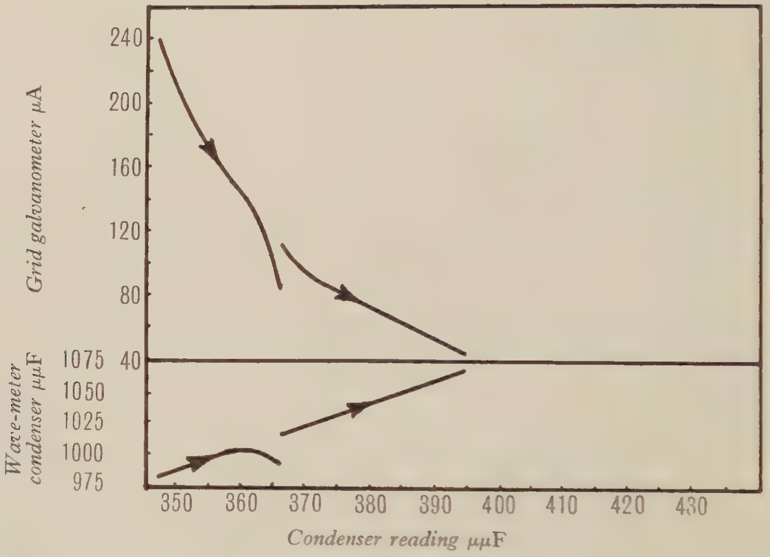

Fig. 6.

The distance between the centres of the coils L_1 and L_2 was then about 13·75 cm. and the magnet faces N and S were about 3 cm. distant from the oscillator. It will be noticed that both the permanent polarising field due to the magnet and the mutual inductance between the grid and anode coils are much less than in the case of the preceding experiments with the longer bar. Otherwise the conditions of the experiments were as nearly as possible identical.

Description of Fig. 6. The curves on this figure are traced from left to right. The discontinuity in the neighbourhood of $C = 366$ μμF is well marked. The frequency corresponding to 1003 μμF on the wave-meter condenser is 540 kc./sec. corresponding to 556 m.

Description of Fig. 7. When the grid galvanometer and wave-meter condenser curves are drawn with decreasing capacity, the discontinuity occurs at a smaller value of *C*. In this case, in contrast to that shown in Fig. 3, there is a sudden drop in the grid current at the stage when the bar assumes control of the frequency.

Probably much higher frequencies could be obtained from thinner and shorter bars by modifying the apparatus. Experiments on the subject are in progress.

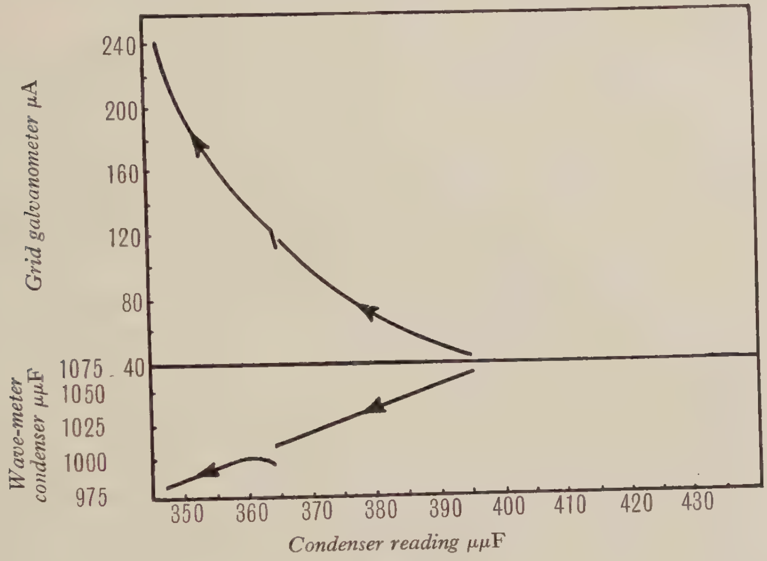

Fig. 7.

DISCUSSION

Prof. R. W. Wood, who was welcomed by the President on behalf of the Society, enquired whether the author had produced oscillations in single crystals, in order to see whether their crystal structure could be affected?

Dr C. V. Drysdale: The magnetostrictive effects mentioned by Dr Vincent are of great interest, but I should like to ask whether the bar was laminated, as at these high frequencies eddy currents must have a very serious influence and it seems probable that a highly laminated specimen would show the effects on a much larger scale than a solid one. The application of magnetostriction to acoustics seems likely to be very valuable, and Dr Vincent is to be congratulated on having shown its possibilities for radio frequencies.

Prof. C. L. Fortescue: The great interest of the paper lies in the fact that the actual range of variation over which the control can be exercised is given numerically, and in Fig. 2. Here, with a range of *C* from 575–620, the arrangement gives practically constant frequency. In other ways, the system behaves exactly like any coupled circuit maintained in oscillation by a self-excited valve.

It would be interesting to know whether the eddy currents take any part in maintaining the oscillations. The penetration under the conditions described is such that

90 per cent. of the changes are confined to less than half a millimetre in thickness. It seems likely that the forces arising from the eddy currents may be about 5 dynes, or thereabouts. If Dr Vincent has any information with regard to the damping, it would be possible to settle whether the phenomena are due to eddies or magnetostriction.

Prof. HOPWOOD: I should like to add my congratulations and to mention that I have succeeded in producing high-frequency oscillations by (apparently) making use of the Johnsen-Rahbek effect.

Dr OWEN: I should like to express my interest in the work of Dr Vincent on the stabilisation of an oscillating valve circuit by use of the phenomenon of magnetostriction. In regard to the question of obtaining constant standards of frequency in radio work, it is natural to compare this method, with its magnetic reaction on the tuned circuit, to the piezo-electric method, with its electric reaction. Has the author any data as to the temperature-coefficient of frequency of his glow-ray rods? His success in obtaining frequencies as high as half a million per second is presumably largely due to the high specific resistance of this material and the consequent reduction of damping due to eddy currents.

One would like to know the interpretation of the particular form of the curves found by the author. It would seem preferable to include the coil L_3 on the condenser side of the tuned circuit CL_1, rather than on the inductance side, since in the latter case the variation with C of the plate current constitutes an unnecessary variation of the polarisation of the bar. The *rise* of frequency of the system as the capacity C is increased seems somewhat paradoxical; perhaps it is due to the oscillatory current growing stronger as C increases over the range BC_1 (Fig. 2), since the effect of increasing the energy of the maintaining system is in general to raise the frequency of the maintained vibration.

Dr ECCLES: I should like to ask Dr Vincent if he has tried to find experimentally a tuned electrical circuit which can be coupled to the valve circuit so as to give discontinuous curves approximately similar to those given by the magnetostrictive oscillator. Such an attempt would bring out the differences between these mechanical systems and the most realisable equivalent electrical system. I must also express the appreciation felt by the audience with regard to Dr Vincent's beautiful and novel experiments.

AUTHOR'S reply: Although measurements of static magnetostriction have been carried out on single crystals of iron*, and of nickel†, I do not know of any work having been done on dynamic magnetostriction with single crystals. My work has been done only with poly-crystalline materials. Prof. Wood's suggestion would form a most promising basis for research by someone familiar with the technique of single crystal growth and X-ray crystallography.

Solid magnetostrictive oscillators must presumably function less efficiently than highly laminated bars having similar elastic properties. The difficulty in applying Dr Drysdale's idea lies in the preservation of the elastic properties of the composite structure. Ordinary transformers hum a note which is due to the forced magnetostrictive vibrations of the laminated structure arising from the varying magnetic field. I hope to find the opportunity of working on the resonant vibrations of laminated oscillators at low frequencies. A split tube of nickel is a convenient low-frequency oscillator, but if one is aiming at a high intensity of sound the gain due to elimination of eddy current losses is largely offset by the decrease in the inertia and restoring forces as compared with those arising in the case of a solid bar.

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* Webster, *Proc. Roy. Soc.* A, **109**, 570–584 (1925); Honda and Mashiyama, *Tohoku University Sci. Rep.* **15**, 755–776 (1926).

† Mashiyama, *Tohoku University Sci. Rep.* **17**, 944–961 (1928).

With regard to the range over which the oscillator controls the frequency of the set, a point commented on by Prof. Fortescue, it should be stated that this varies very much with the constants of the apparatus. I have been in the habit of picturing the oscillating bar and its coil as constituting a system approximating to Butterworth's Class A*. If this is legitimate, then the bar and its coil could be replaced by a coil in series with a parallel combination of L, C and R. The eddy current loss could be allowed for by another inductance with mutual inductance to the coil of the bar in series with a resistance. The L of the equivalent circuit must be pure and thus it seems impossible to reproduce the effects of the oscillating bar by the substitution of a real circuit which is to be its equivalent at all frequencies. Electromagnetic deforming forces must be in operation when the bar is solid or when an unsplit tube is used as an oscillator. I am inclined to think that such forces, though perhaps not negligible, are very small compared with those due to magnetostriction. The reasons for this are that the oscillators which show the most striking effects are those such as nickel and its alloys, and iron and its alloys, which are known to have high coefficients of the direct static magnetostrictive or Joule effect. I have succeeded in getting distinctly audible sound from a bar of commercial aluminium which I attributed to magnetostriction†, but I am now not certain that the results should not be regarded as due to the forces of electromagnetic origin contemplated by Prof. Fortescue. I have not succeeded in getting any such effects with brass. I hope to return to experiments on these matters, which are profoundly obscure though exceedingly interesting.

The evaluation of damping to which Prof. Fortescue refers might probably be effected by methods similar to those used by Dye in his researches on crystal resonators‡.

I am interested to hear of Prof. Hopwood's experiment and hope that he will give a fuller account of the work to the Society. It seems that Prof. Hopwood has added a new method of electrically maintaining a high-frequency mechanical vibration to those already known.

Prof. Pierce§ has published data which answer Dr Owen's first enquiry. I understand that "glow-ray" and "nichrome" are practically synonyms. Nickel is, I think, just as suitable as glowray except that, according to Pierce, it has a higher temperature coefficient of frequency.

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* *Proc. Phys. Soc.* **27**, 410–424 (1915).

† *Electrician, loc. cit.*

‡ *Ibid.* **38**, 399–458 (1926).

§ *Loc. cit.*

Dr Owen suggests putting the bar and coil in the condenser branch of the oscillatory circuit. In the interval between the preparation of the paper for the press and its reading before the Society, I had carried out a series of experiments on the 6 mm. glow-ray bar intended to throw light on the comparative behaviour of an oscillatory circuit when the bar and coil were switched into either of its branches. The pivot of the two-way switch was joined to the negative terminal of the high-tension battery and the ends of the coil L_3 (Fig. 1) were connected to the other two electrodes of the switch. One of these was joined to L_1 and the other to C so that on moving the switch arm L_3 could be thrown into either branch of the anode fly-wheel. The coil L_1 was changed for a similar one of 30 turns of No. 24 D.W.S. copper wire. The other conditions were as given in the paper. The grid coil and main inductance coil had to be more closely coupled when L_3 was put in the capacitative branch than when in the inductive branch. The centres of the coils were 4·2 cm. and 5·9 cm. apart in the two cases. The comparison is thus not strictly between the two positions of L_3 but includes effects due to the altered position of the grid coil. The results as regards control can be seen from the following table:

		Capacity $\mu\mu F$		Range
Capacity decreasing	L_3 in capacitative branch	487	507	20
	,, inductive ,,	448	458	10
Capacity increasing	L_3 in capacitative branch	487	528	41
	,, inductive ,,	448	484	36

In this particular series of experiments the control is greater when the bar and coil are in the condenser branch. The peaks of the grid current curves are also more pronounced. In addition to the advantage of constant polarisation the arrangement has the convenience that the sense of winding of L_3 is immaterial.

In reply to the President: I have not done any experiments on the imitation of the effects of the oscillator by means of a coupled circuit. Although such a circuit could not, I think, quite adequately replace the bar, the suggested experiments would be very interesting. One reason why I have not tried such substitution experiments is that I know of no ready means of efficiently clamping and unclamping an oscillator. This applies to large bars and small ones. Any clamping method I have tried is somewhat tedious in that on unclamping it is difficult to reproduce the exact conditions which existed before clamping.

I wish to thank the President and those Fellows who took part in the discussion for the interest they showed in the paper and for their very kind congratulations.

THE ABSOLUTE MEASUREMENT OF SOUND INTENSITY

By F. D. SMITH, M.Sc., Admiralty Research Laboratory, Teddington

Communicated by Dr A. B. Wood April 9, 1929.
Read and discussed June 28, 1929

ABSTRACT. An absolute measurement of sound pressure is described in which the sound is received with a moving-coil receiver. The signal heard after suitable amplification is compared with the signal produced by a small known electromotive force v applied to the receiver. It is shown that when the two signals are equal in intensity the following simple relation connects the total sound pressure P on the receiver with the electromotive force v,

$$P = vHl/z_m,$$

where H is the strength of the magnetic field in which the moving coil, consisting of a length l of wire, moves, and z_m is the motional impedance of the receiver at the frequency of the sound. It is shown that the phase also of the sound can be determined with the aid of a phase-shifting transformer. Since the measurement is independent of the amplifying circuit, it is possible to use a high degree of amplification and very feeble sounds may therefore be measured.

§ 1. INTRODUCTION

Methods of measuring sound intensity may be roughly classified into two groups, those in which a directly measurable effect is produced by the sound and those in which the unknown sound pressure is compared with a known force, produced electrically. The classical methods are included in the first group, for example, the Rayleigh disc where the sound produces a measurable torque on a suspended disc*, and the torsion pendulum where the radiation pressure of sound on a reflecting obstacle in its path is measured. Langevin† and Boyle‡ have used the torsion pendulum for the measurement of intense high frequency sounds in water. Tucker and Paris§ have made absolute measurements of sound intensity by measuring the change of resistance of a thin hot wire in a sound field. Unfortunately, a very intense sound is needed to produce directly measurable effects, and resonators must often be used to reinforce the sound. Even with the help of resonators, the direct methods are limited to fairly loud sounds. For the measurement of feeble sounds, one of the methods of the second group must be used. The compensation method proposed by Gerlach[*] is a typical example. A metal strip exposed on one side to the sound waves lies between the poles of a magnet. The pressure of the sound on the strip sets it into vibration and an alternating current is passed through the strip of such magnitude, frequency and phase that it brings the strip to rest. The sound pressure on the strip is then equal to the electromagnetic force on it, which can be calculated from the known current and magnetic field. Very sensitive arrangements for detecting the motion of the strip have been devised. A similar compensation method in which the sound pressure is balanced against the electrostatic force between the plates of a condenser microphone is described by Meyer[†].

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* Lord Rayleigh, *Theory of Sound*, **2**, 44–45 (1896).

† Langevin, *International Hydrographic Bureau, Monaco: Special Papers*, No. 3, 1924; No. 4, 1926.

‡ R. W. Boyle, *Proc. Roy. Soc. Canada*, III, 167 (1925).

§ Tucker and Paris, *Roy. Soc. Trans.* **221**, 389 (1921).

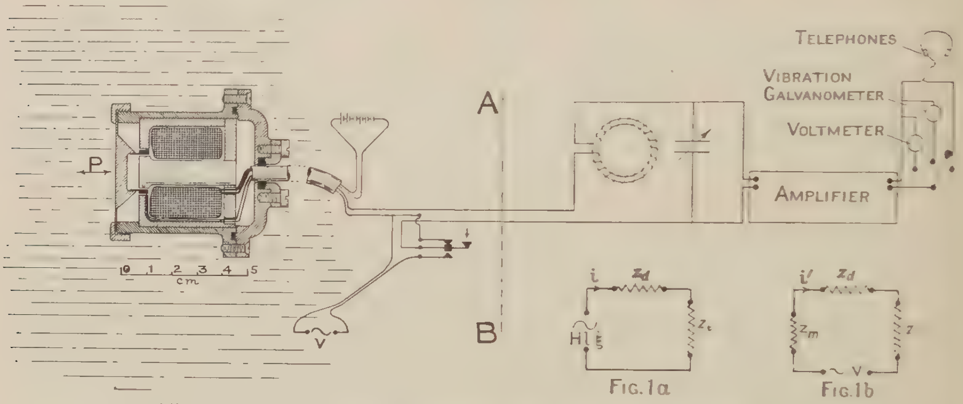

Fig. 1. Circuit diagram for measurement of sound pressure.

The method described here resembles those of Gerlach and Meyer in that it depends upon a balance between the effects produced on a sensitive amplifying circuit by the unknown sound wave and a known small electromotive force. A moving-coil receiver, shown in Fig. 1, is connected to a sensitive receiving circuit consisting of a tuned circuit and a multistage valve amplifier. A sound wave falling upon the receiver produces a deflection of a voltmeter, or a vibration galvanometer, or a note in telephones connected to the output of the valve amplifier, the choice of indicating instrument depending on the frequency of the sound to be measured. Arrangements are made for applying to the receiver a small known electromotive force of the same frequency as the sound wave. The sound wave and the electromotive force act alternately, and the magnitude of the latter is adjusted until both produce the same deflection of the indicating instrument. It can be shown that when this condition is fulfilled a simple formula gives the magnitude of the sound pressure on the receiver in terms of the known electromotive force and three easily measured constants of the receiver. These constants are the length of wire in the moving coil, the strength of the magnetic field in which it moves and its motional impedance at the frequency of the sound wave. To find the formula it is necessary to calculate separately the effects of the sound pressure and the electromotive force.

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[*] Gerlach, *Wiss. Veröff. aus d. Siemens-Konzern*, 3, 139 (1923); *Handbuch der Physik* 8, *Akustik*, pp. 572–580 (Springer, 1927).

[†] E. Meyer, *Zeits. Tech. Physik*, 7, 609–616 (1926).

§2. EQUATIONS OF MOTION

The receiver shown in Fig. 1 is suitable for the reception of sound in water, but it can represent any moving-coil receiver receiving sound in any medium. It consists of a rigid circular piston of effective area A supported on an elastic edging which resists a displacement ξ with a force $G\xi$. A coil of a length l of wire rigidly attached to the piston lies in a magnetic field of strength H. The effect of the medium in contact with the piston can be represented by an addition to its mass of M_w and a damping force $N_w\dot{\xi}$. When the piston moves with simple harmonic motion with instantaneous velocity $\dot{\xi}$ the medium opposes the motion with a force

$$M_w\ddot{\xi} + N_w\dot{\xi}.$$

Let P represent the total force on the piston due to a sound wave falling on it when it is prevented from vibrating, where

$$P = P_0 e^{j\omega t}.$$

This force becomes

$$P - M_w\ddot{\xi} - N_w\dot{\xi},$$

when the piston is released and begins to vibrate with velocity $\dot{\xi}$. It has to overcome the inertia M of the piston and the coil, the stiffness G of the coil support, the internal mechanical friction N_i and the electromagnetic force on the coil. The equation of motion is therefore

$$P - M_w\ddot{\xi} - N_w\dot{\xi} = M\ddot{\xi} + \mathrm{N}_i\dot{\xi} + G\xi + Hli,$$

where i represents the instantaneous current flowing in the coil. When the equation is re-written

$$P = (M + M_w)\,\ddot{\xi} + (N_w + N_i)\,\dot{\xi} + G\xi + Hli,$$

it becomes clear that it can be expressed in the form

$$P = Z\dot{\xi} + Hli \qquad \text{......(1)},$$

because $\ddot{\xi} = j\omega\dot{\xi}$ and $\xi = \dot{\xi}/j\omega$ for simple harmonic motions. Z represents the total mechanical impedance of the receiver. An equation can be obtained relating the current i flowing in the coil to the velocity of the coil. The current i depends upon the impedance of the external circuit to which the coil is connected. The whole of the receiving circuit to the right of the line AB in Fig. 1 can be represented by a complex impedance z_e, and the whole circuit takes the simple form shown in Fig. 1 (*a*), in which z_d represents the damped impedance of the coil, that is, its impedance when motion is prevented, and $Hl\dot{\xi}$ is the electromotive force induced by the motion of the coil in the magnetic field. We may write

$$Hl\dot{\xi} = (z_d + z_e)\,i \qquad \text{......(2)},$$

and $\dot{\xi}$ may be eliminated from (1) with the following result,

$$P = \{Z\,(z_d + z_e)/Hl + Hl\}\,i \qquad \text{......(3)}.$$

This equation gives the current i flowing to the external circuit when a force P, due to the sound, acts on the receiver.

When the electromotive force v acts upon the circuit instead of the sound pressure, a current i' flows in the external circuit depending upon the total electrical impedance. The whole circuit is equivalent to that of Fig. 1 (*b*) in which the motional impedance z_m of the moving coil must be included because the current i' sets the coil into vibration. We may write

$$v = (z_d + z_m + z_e)\, i' \qquad \text{......(4).}$$

The indicating instrument at the output of the amplifier gives the same reading for the sound pressure P and the electromotive force v when $i = i'$, that is when

$$\frac{P}{Z\,(z_d + z_e)/Hl + Hl} = \frac{v}{z_d + z_m + z_e} \qquad \text{......(5),}$$

from equations (3) and (4).

This relation between P and v can be simplified by eliminating Z or z_m as follows. A current i' in the coil of the receiver results in a mechanical force Hli' which sets the coil into vibration with a velocity $\dot{\xi}$ of magnitude Hli'/Z. This motion of the coil in the magnetic field induces in it an electromotive force of $Hl\dot{\xi}$, that is H^2l^2i'/Z, which must be equal to $z_m i'$ by the definition of motional impedance. Therefore

$$z_m = H^2l^2/Z \qquad \text{......(6).}$$

§ 3. RELATION BETWEEN SOUND PRESSURE AND ELECTROMOTIVE FORCE

The result of eliminating Z from (5) by means of (6) is

$$P = vHl/z_m \qquad \text{......(7),}$$

and the result of eliminating z_m is

$$P = vZ/Hl \qquad \text{......(8).}$$

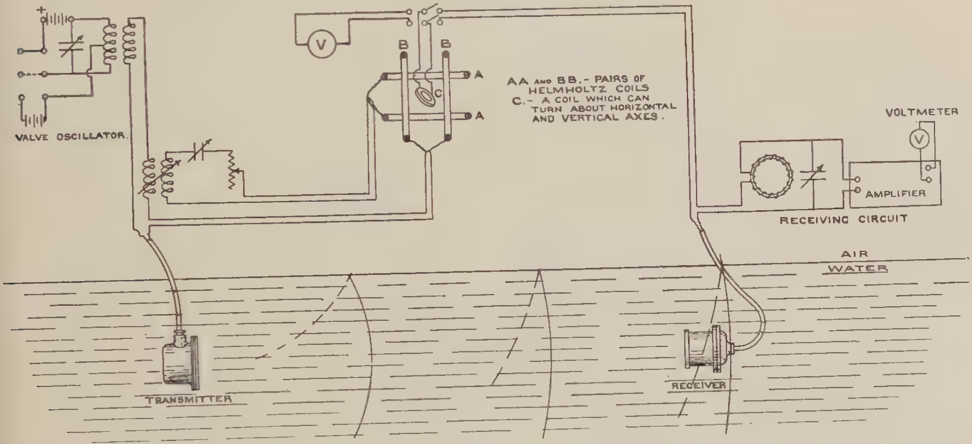
These are the two formulae upon which this method for the absolute measurement of sound pressure depends. The first involves z_m, the motional impedance of the moving coil, and the second involves Z, the total mechanical impedance of the receiver. If the receiver is resonant at the frequency of the sound, its motional impedance is easy to measure and (7) is used. If the receiver is resonant at a frequency much higher or lower than that of the sound, this motional impedance is too small to measure and it is necessary to determine the mechanical impedance Z. From the equation of motion (1),

$$Z = j\omega\,(M + M_w) + (N_w + N_i) + G/j\omega,$$

where $j = (-1)^{\frac{1}{2}}$ and $\omega = 2\pi \times$ frequency. Z is very nearly equal to $j\omega\,(M + M_w)$ when the resonance frequency of the receiver is much lower than the frequency of the sound, and very nearly equal to $G/j\omega$ when it is much higher. In the first case the effective mass of the vibrating parts of the receiver is required, and in the second case the stiffness of the support. Both of these quantities can be found with sufficient accuracy provided that the receiver is suitably designed.

The resonant receiver is a very sensitive arrangement, but it is limited to the narrow range of frequency in the neighbourhood of its resonant point where the motional impedance is appreciable. The non-resonant receiver can be used over a wide range of frequency, but it is relatively insensitive, a disadvantage which can be partly overcome by the use of a receiving circuit giving a high overall amplification.

It is worthy of note that the impedance of the external circuit z_e and the damped impedance of the moving coil do not appear in equations (7) and (8), a somewhat unexpected result since the amplitude of vibration of the receiver does depend upon the impedance of the circuit connected to it. The measurement is independent of these impedances and any convenient amplifying circuit may be used. In particular, the resistances in the leads connecting the receiver to the amplifying circuit do not affect the measurement, and the amplifier may be placed at a convenient distance from the region in which the sound waves are travelling.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A
C
AA AND BB.- PAIRS OF HELMHOLTZ COILS
C.- A COIL WHICH CAN TURN ABOUT HORIZONTAL AND VERTICAL AXES.
VALVE OSCILLATOR.
VOLTMETER
V
AMPLIFIER
RECEIVING CIRCUIT
AIR
WATER
RECEIVER
TRANSMITTER

Fig. 2. Phase and amplitude measurement with a phase-shifting transformer.

The measurement gives the total sound pressure on the receiver when it is prevented from vibrating. In some special cases the sound pressure p per unit area in the medium when the receiver is removed can be inferred. If the dimensions of the receiver are small compared with the wave-length of the sound, the pressure p is given by

$$P = pA,$$

where A is the area of the vibrating face of the receiver. If a receiver of any size is supported by a large rigid plane plate on which the sound falls normally, the pressure is doubled by reflection and

$$P = 2pA.$$

Finally, a receiver with a plane receiving surface large compared with the wave-length on which the sound falls normally is subject to a total pressure P, where

$$P = 2pA.$$

These are the only three cases from which the sound pressure in the undisturbed medium can immediately be inferred from the sound pressure on the receiver. Receivers comparable in size with the wave-length are subject to a total pressure

P which lies between the values pA and $2pA$. The calculation of the exact value involves the calculation of the diffraction and scattering of sound by the receiver considered as an obstacle in the path of the sound. The solution given by Rayleigh for a spherical obstacle has been applied by Ballantine* to sound intensity measurements with a condenser microphone. He supported the microphone inside a spherical case so that its receiving surface formed part of the surface of the sphere, and, by calculating the diffraction and scattering of sound by the sphere, found the pressure on the microphone in terms of the pressure in the undisturbed medium. He was thus able to use a receiver comparable in size with the wave-length for the absolute measurement of sound intensity.

§4. MEASUREMENT OF MAGNITUDE AND PHASE

The relations between P and v given in equations (7) and (8) hold when both produce the same current in magnitude and phase in the external circuit. If the phase of v is changed by half a period, the current produced by it changes in phase by the same amount and becomes opposite in phase to the current produced by P. The application of P and v simultaneously to the circuit then produces no current in the external circuit and a null measurement results. By varying v in magnitude and phase until there is no deflection at the output of the amplifier, a balance between P and v is obtained which is expressed by the relations

$$P = -vHl/z_m \quad \text{......(9),}$$

and

$$P = -vZ/Hl \quad \text{......(10),}$$

from either of which the magnitude and phase of P can be calculated.

The alternating electromotive force variable in magnitude and phase can be obtained from an alternating current potentiometer. The instruments in which the magnitude and phase of the known electromotive force are separately variable are more convenient for sound measurements than those which resolve the electromotive force into two components at right angles†. The conversion of the rectangular components to polar components is inconvenient when many readings have to be made. For this reason the phase-shifting transformer shown in Fig. 3 has been designed to provide the variable electromotive force. It may safely be used at the highest sonic frequencies, as the use of metal in its construction is avoided. A pair of equal co-axial circular coils at a distance apart equal to their radius is fixed at right angles to another similar pair of coils. When one pair of coils carries an alternating current equal to but in quadrature with the current in the other pair of coils, a rotating magnetic field is produced inside the arrangement. A movable coil supported in this rotating field can be turned about horizontal and vertical axes. The rotation of the coil about a horizontal axis controls the magnitude of the electromotive force induced in it, and its rotation about a vertical axis controls the phase. The disposition of each pair of fixed coils is that shown by Helmholtz to produce a fairly uniform field in the space in which the movable coil lies. The range of electromotive force obtained by rotating the movable coil about a horizontal axis is extended by providing coils with various numbers of turns. The sets of standard coils sold for broadcast reception are suitable for this purpose, as they have the same overall dimensions and are readily interchangeable in the phase-shifting transformer. In another convenient arrangement for changing the range of the instrument, the fixed coils are wound in two parts which can be connected in series or in parallel and, further, each pair of fixed coils may be in series or in parallel. These changes are sufficient to provide a very wide range of electromotive force.

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* Stuart Ballantine, "Effect of diffraction around the microphone in sound measurements," *Phys. Rev.* **32**, 988, 992 (1928).

† A. Campbell, "A new alternating current potentiometer of Larsen type," *Proc. Phys. Soc.* **41**, 94–8 (1928). See the discussion. C. V. Drysdale, *Proc. Phys. Soc.* **21**, 561–571 (1909); *ibid. Electrician*, **75**, 157–160 (1915).

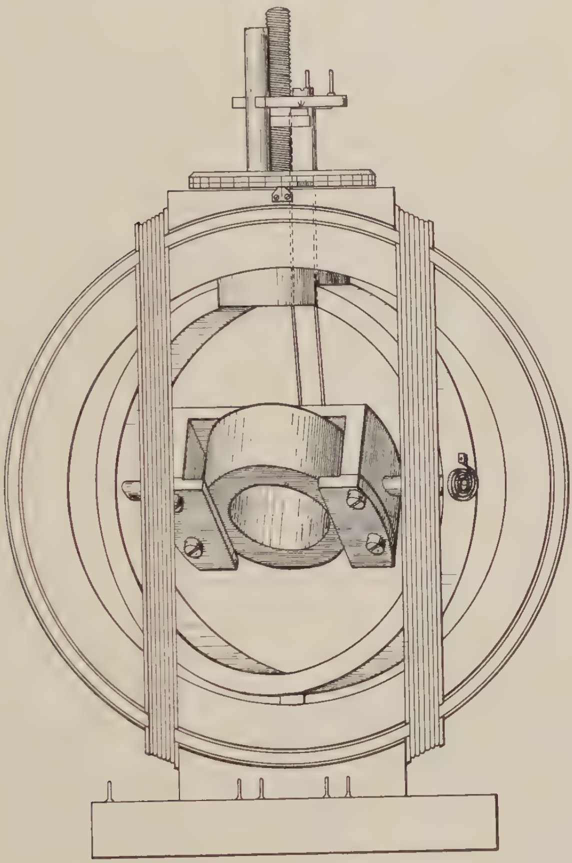

Fig. 3. Phase-shifting transformer.

The movable coil is carried on a vertical wooden ring which rotates about a vertical axis inside the fixed coils, its angular position being shown on a circular scale and pointer at the top of the instrument. The electrical connections to the movable coil are made by two flexible conductors running from the coil through the top of the instrument to a pair of terminals. These terminals are fixed in a block, and by the raising and lowering of this block with a screw micrometer the coil can be turned about a horizontal axis. Two spiral springs, one of which is seen in Fig. 3, turn the coil against its electrical connections and keep the latter taut, thus preventing any back-lash. The micrometer reading is easily converted into the corresponding circular position of the coil. Wood and ebonite are used in the construction of the instrument, metal being avoided as much as possible because of its effect in distorting the magnetic field.

The external electrical connections to the instrument are shown in Fig. 2, where the instrument itself is drawn diagrammatically in plan. One pair of fixed coils carries the same current as the source of sound, while current for the other pair of coils is derived from a mutual inductance and a resonant circuit. When this circuit is adjusted to resonance, the currents in the two pairs of coils are in quadrature and can now be made equal by adjustment of the variable resistance in the resonant circuit. To test the adjustment of the two currents for equality and quadrature the movable coil is connected to a voltmeter and the deflections as the coil is rotated about a vertical axis are observed. The deflection of the voltmeter should be independent of the angular position of the moving coil. In the practical use of the instrument this condition is found by trial, and then calibration is carried out with the aid of the voltmeter and an ammeter in series with the fixed coils.

The magnitude and phase of the electromotive force which balances the sound pressure are known from the calibration and the geometry of the phase-shifting transformer. It remains to infer the magnitude and phase of P from equation (9) or (10). Writing

$$P = P_0 e^{j\omega t},$$

$$v = v_0 e^{j(\omega t - \alpha)},$$

and

$$z_m = |z_m| e^{j\beta},$$

where $j = (-1)^{\frac{1}{2}}$, $\omega = 2\pi \times$ frequency, $|z_m|$ represents the magnitude of the motional impedance and tan β is the ratio of motional reactance to motional resistance it appears from (9) that

$$P_0 = -\frac{v_0 H l}{|z_m|} \times e^{j(\alpha - \beta)} \qquad \text{......(11)},$$

which shows that

$$\alpha - \beta = \pi,$$

and

$$P_0 = v_0 H l / |z_m|.$$

Since the angle β is known from the motional impedance, the angle α which is the phase difference between the sound pressure and the electromotive force is also known. For the special case of a receiver used at its resonance point, the motional impedance reduces to a pure resistance, β is zero and the sound pressure and the electromotive force have opposite phases. Similar formulae for the magnitude and phase of P can be derived from (10) if the receiver is to be used at a frequency remote from its resonance point.

It is often sufficient to measure sound pressure regardless of phase: a source of known small electromotive force of the same frequency as the sound to be measured is required. Davis and Littler* used a calibrated mutual inductance, through the primary of which they passed the alternating current to their source of sound. When the source of sound is mechanically driven or at an inconveniently large distance from the receiver, it is necessary to provide a separate valve oscillator generating the small electromotive forces. A suitable circuit has been described by the author with B. S. Smith†, and in the same place references to other methods of producing small known electromotive forces will be found. The phase of the sound being measured is in this case meaningless, and the null measurement in which the sound pressure is balanced against the electromotive force cannot be used. The sound pressure and the electromotive force must be applied alternately to the receiving circuit, and the electromotive force adjusted until both produce the same deflection of the indicating instrument.

Measurements of phase only are easily made with a microphone receiver, that is, a receiver in which the pressure changes periodically the resistance of carbon granules. The microphone is supplied not with direct current in the usual way but with alternating current of the same frequency as the sound, from a phase-shifting transformer. Let $(R_0 + R_1 \sin \omega t)$ represent the microphone resistance, the alternating term representing the effect of the sound falling on it, and let $i_0 \sin (\omega t + \alpha)$ represent the alternating current supplied to it. The potential difference between its terminals is

$$(R_0 + R_1 \sin \omega t) \times i_0 \sin (\omega t + \alpha),$$

or

$$R_0 i_0 \sin (\omega t + \alpha) - \tfrac{1}{2} R_1 i_0 \{\cos (2\omega t + \alpha) - \cos \alpha\},$$

and this has a steady component of $\frac{1}{2} R_1 i_0 \cos \alpha$. A direct current galvanometer connected in series with the microphone is therefore deflected by an amount proportional to $\frac{1}{2} R_1 i_0 \cos \alpha$. If the phase of the current supplied to the microphone is adjusted to quadrature with the periodic change of microphone resistance, α becomes 90°, $\cos \alpha$ becomes zero and the deflection of the direct current galvanometer is brought to zero. A null method of phase measurement is obtained in which the galvanometer is used to adjust the current supplied to the microphone to quadrature with the periodic change of microphone resistance. It is to be noted that there is a constant phase difference between the sound pressure on the microphone and the periodic change of microphone resistance, depending upon the mechanical constants of the microphone. The changes of phase as the microphone is moved about in the sound field can however be easily and quickly measured.

§ 5. ACKNOWLEDGMENTS

The author desires to express his indebtedness to the Admiralty for permission to publish this paper, and to Mr B. S. Smith for his inception of the microphone phase-measuring device and valuable suggestions and advice concerning the phase-shifting transformer.

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* "The measurement of transmission and reflection of sound by partitions," *Phil. Mag.* 3, 181 (1927).

† "An instrument for the production of known small high frequency alternating electromotive forces," *Proc. Phys. Soc.* **41**, 18–28 (1928).

DISCUSSION

Dr C. V. Drysdale: I should like to congratulate the author, as a member of my own scientific staff, on his contribution to a subject of great and growing importance. In spite of the enormous development of acoustics in connection with telephony and sound reproduction, acoustic measurement is still in its infancy, and we are much in the same condition as electrical engineers were before the advent of ammeters and voltmeters. Acoustic vibrations are easily convertible into electrical ones, but the two great difficulties are the extremely small power available and the uncertainty as to the amount of it converted, owing to the reflecting properties of the receiver and the disturbing effect of its presence in the wave-fronts. For these reasons, absolute acoustic measurements are exceptionally difficult, and, although certain methods have been devised which are beautiful in theory, their use is attended with great difficulties and uncertainties. The author's contribution to this problem is certainly a valuable one and does give an absolute measurement of the pressure on the receiver piston, regarded as a rigid surface, by a comparatively simple and accurate method, although a factor of between 1 and 2 must be applied depending upon the ratio of the diameter of the piston to the wave-length of the sound. Care must of course be taken, in cases where the diameter is large, that the receiver face is perpendicular to the direction of propagation, but this merely requires turning it until the e.m.f. is a maximum. As an old worker with phase shifting transformers, I should also like to express appreciation of Messrs B. S. and F. D. Smith's simple and convenient phase shifter, with its device for varying the magnitude as well as the phase of the secondary e.m.f.

Mr A. S. Radford: I should like to call the author's attention to the fact that, besides the obstacle effect of the microphone itself, we have errors due to reflection from other obstacles, such as room walls, which cannot be eliminated and are in general greater than those caused by the presence of the microphone. I should be greatly obliged if the author would tell us if his transmitter is intended for use over the whole audible frequency range, or only to measure the distribution of intensity around a source for a single frequency. It would seem that for low frequencies especially this type of microphone would be less sensitive than, say, the condenser transmitter.

Mr W. West: The method aims at a measurement of the total alternating force exerted on the piston. The author mentions the desirability of interpreting the results in terms of pressure in the unobstructed sound field. For this purpose it is necessary to stipulate that the sound emanates from a single source, i.e. that measurements are made in open air or the acoustical equivalent, since the presence of reflecting surfaces, in effect, increases the number of sources of sound. For all work where sustained pure tones are to be measured (e.g. in obtaining frequency characteristics of loud speakers), both the calibration and the use of the sound detector should be effected under this condition, otherwise the instrument may fail to give a measure, not only of intensity but also of pressure, with any degree of accuracy. It is assumed that the piston, together with its attachment to the moving coil, is rigid. There will, I think, be practical difficulties, especially when dealing with the more acute audible frequencies, in the design of a suitable mechanical structure whose effective mass is sufficiently small to permit reasonable sensitivity while its rigidity can be relied upon at such frequencies. I am referring in particular to the measurement of sound in air.

Mr A. J. ALDRIDGE: The method described by the author is really a modification of the Gerlach compensator, but he avoids one of the chief difficulties of the Gerlach method, namely, the determination of the balance point—at any rate in those cases (and they are far the most numerous) where the magnitude of the sound and not its phase is required. The author has deduced a very simple formula to determine the acoustic pressure, but it is always advisable whenever possible to obtain confirmatory results. No information is given as to whether any have been obtained. Dr Drysdale appears rather contemptuous of the other methods of measuring sound. In the Post Office Research Laboratories, Rayleigh discs are in almost daily use for sound measurement and are found entirely satisfactory. They are robust and easily made, calibrated and used. In Germany a modified Gerlach compensator is found very satisfactory, and in America and in the C.C.I. Laboratory in Paris thermophones are in constant use. Good agreement is obtained between calibrations by these various methods, and I would like to ask the author if he has made any comparisons between his method and others, and, if so, with what result?

Dr A. B. WOOD: To those who appreciate the practical difficulties of sound-intensity measurement, the paper will come as a valuable contribution to the subject. In addition to this, it serves as a good example of the modern tendency to develop the theory of mechanical oscillatory systems on electrical lines, a tendency to which the President drew attention in his address to the Society a short time ago. The paper gives us a very simple method of determining the absolute pressure-amplitude in the medium, in the absence of the receiver. Certain limitations are necessarily imposed. In the first place, the wave form must be sinusoidal, for the receiver, regarded as an obstacle, must fulfil certain conditions with respect to its dimensions relative to a wave-length of the sound. A receiver would therefore behave differently as an obstacle towards the higher harmonics and the fundamental. A receiver to deal with complex sounds would on this account have to be large compared with a wave-length of the fundamental, or small compared with the wave-length of the highest harmonic. It is pleasing to note that the author has drawn attention to the relation between the effective pressure and the size of the receiver, a point which hitherto has been entirely overlooked by many writers on the subject. A complex wave form would also introduce additional complications into the electrical method of measurement which is described in the paper. It would appear also that the method, although theoretically applicable to frequencies far removed from the resonant frequency of the receiver, would in practice be inaccurate at such frequencies, owing to the difficulty of measuring very small values of the motional impedance z_m. In the introduction to the paper the author refers to the null method of measuring sound intensity by means of the Gerlach strip receiver. I should like to have his opinion regarding the advantages which he claims for his own method over that of Gerlach and Meyer. I conclude by congratulating him on a very nice piece of work. It is to be hoped that he will extend his treatment of the subject to other types of receiver.

AUTHOR'S reply: The work described in my paper was carried out with a view to measurements of sound intensity in water. The Rayleigh disc and the condenser microphone recommended by Mr Aldridge for measurements in air are inadequate in water, the former being inconvenient and the latter insensitive. The difficulties which have to be overcome are not the same for the two media. For example, the mass of water associated with a small rigid piston of, say, 3 cm. radius vibrating in an aperture in a rigid plate is 72 gm. and the corresponding mass of air is only 0·0864 gm. As there are in any case 72 gm. of water associated with the piston and moving coil, there is no point in making it light and therefore no difficulty in making it rigid. On the other hand, a piston and moving coil for use in air must be light and rigid, two conflicting requirements not easily satisfied. Mr West will see that in choosing water as the medium, I have escaped this difficulty.

I cannot describe at length the extensive experiments on sound-intensity measurements carried out at the Admiralty Research Laboratory, but at Mr Aldridge's request I have selected one experiment of special interest for a short description. This test, which was suggested by Mr B. S. Smith, will be recognised by electrical engineers as the acoustical equivalent of the Hopkinson test for a pair of similar direct current machines in which one, used as a motor, drives the other, used as a generator. I placed two exactly similar moving-coil instruments, facing each other at a distance of about 12 ft., in a large tank of water, and used one to generate sound and the other to receive it. I measured and calculated the efficiency of the generator, inferred from the results the efficiency of the receiver, and finally calculated the current which should flow in the coil of the receiver when a known current was supplied to the generator. As the measured current in the coil of the receiver agreed closely with the calculated value, it was clearly safe to use the instruments as receivers for sound-intensity measurements. I feel sure that Mr Aldridge will agree that a calibration of this kind is sufficiently exacting and has, moreover, the advantage that it is self-contained. It has an obvious application in the determination of the frequency characteristics of pairs of loud-speakers in air.

The essential difference between my method and that of Gerlach is that I obtain a balance between the effect of a sound pressure and an electromotive force by reducing the current in the moving coil to zero, whereas Gerlach does so by reducing the motion of the moving coil to zero. In reply to Dr A. B. Wood's question as to the relative merits of the two methods, I think it is sometimes more convenient to detect a small electric current rather than a small mechanical vibration. His objection that the motional impedance z_m is very small at frequencies remote from resonance can be met by measuring the effective mechanical impedance Z instead and using formula (8).

Mr Radford and Mr West have emphasised the confusion which arises from the presence of reflecting surfaces in the vicinity of the measuring apparatus. Even in open air and in the sea the reflections from the ground and the surface of the sea are an unmitigated nuisance. The difficulty which is common to all sound-intensity measurements can be partly avoided by the use of directional transmitters and receivers and sound-absorbing materials.

In reply to Mr Radford, the transmitter shown in Fig. 1 is suitable for sonic frequencies in water but not in air. It should be possible to fit a moving-coil loudspeaker with a more rigid piston for use in air and to compensate for the loss of sensitiveness by increased amplification.

THE MEASUREMENT OF THE VISCOSITY OF GLASS AT HIGH TEMPERATURES BY THE ROTATING CYLINDER VISCOMETER

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Communication from the Staff of the Research Laboratories of the General Electric Company, Limited, Wembley

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ABSTRACT. After reviewing previous work on the subject, the paper describes an apparatus in which the molten glass is contained in a cylindrical sillimanite pot provided with a coaxial cylindrical stirrer which is caused to rotate: the viscosity is inferred from the angular velocity produced in the stirrer by a measured torque. The apparatus was calibrated by measurement with it of the viscosities of golden syrup and pitch, these quantities being also measured independently with a falling sphere viscometer and by a torsion method respectively. The calibration factor of the authors' apparatus appears to be independent of the viscosity over a wide range. The authors' results and those of previous workers are considered to be in reasonable agreement with one another when allowance is made for differences in composition of the samples used.

§ 1. INTRODUCTION

The measurement of the viscosity of glass at high temperatures involves considerable experimental difficulties.

Valuable work has been done by Washburn and Shelton (1), English (2), Stott (3), and Gehlhoff and Thomas (4). As the glasses used by the above workers have not the same chemical composition, a direct comparison of their measurements is not possible. Further difficulty arises in view of the fact that the published compositions of the glasses are not all chemical analyses.

Washburn calculated the composition of his glasses from the known composition of three of them, which were mixed in varying proportions, and even so all the minor constituents were neglected. Gehlhoff and Thomas calculated their glass compositions from the batch formula and this gives rise to some uncertainty. Furthermore, they have published their results in a rather different form, and the scale of the diagrams is so small that additional uncertainty is introduced when the data are read from the curves.

English and Stott give the analysis of the glass actually used.

One or two other points arise in comparing the published data, but these are dealt with later in the paper in the appropriate sections.

An approximate comparison between the results obtained by Washburn, English and Stott has been made by Stott in one case, where the three workers give data for glasses of approximately similar composition. This will be dealt with, in more detail, later.

The lack of agreement shown by Stott's comparison, and the importance of the subject, have encouraged the authors to attempt a further study of the problem.

Washburn, English, and Gehlhoff and Thomas all used viscometers of the concentric cylinders type applying a given torque to the inside cylinder and measuring its speed of rotation, the outside cylinder being rigidly held.

Stott (5) measured the viscosity of glass from the founding temperature down to about 1000° C. by determining the rate at which a platinum-iridium sphere attached to the end of a platinum-iridium wire was raised through the glass under a given force.

In a later work (6) he determined the viscosity of glass by weighing the quantity of glass carried on a platinum-iridium wire withdrawn at a definite rate from a pot of glass maintained at a constant temperature, utilising the principle developed by Goucher and Ward (7) at these Laboratories for the coating of fine wires with various suspensions.

As previously mentioned, an approximate comparison between the results of English, Stott and Washburn has been made by Stott (8) for glasses of approximately similar compositions. His results are reproduced in Fig. 1.

The curves represent the results of the three workers on glasses of the compositions shown in Table I.

Table 1. Analyses of the glasses compared by Stott

	Stott, N.P.L. 15	English, No. 6	Washburn
SiO_2	72·22	73·18	72·22
Al_2O_3	0·71	0·58	—
Fe_2O_3	0·11	0·61	—
CaO	6·94	6·26	8·29
MgO	0·53	0·21	—
Na_2O	19·49	19·38	19·49

The curve marked "English" was obtained by Stott from English's figures for his glass No. 6 after applying a small correction, derived from Washburn's isokoms, to allow for the slight differences in composition. In the making of this adjustment, the corrections were calculated from the percentages of soda and silica only. The circles slightly above the curve are English's actual points. Washburn's curve was derived from his isokoms.

From Fig. 1 it is seen that whilst the curves of English and Stott are approximately parallel at the lower temperatures, they diverge considerably at the higher temperatures, English's curve becoming much flatter than Stott's. It is also noticed that Washburn's curve has a much steeper slope than either of the other two.

In calculating the viscosity from his measurements, Washburn used a calibration factor which varied over a wide range (approximately 3 to 1) with the viscosity,

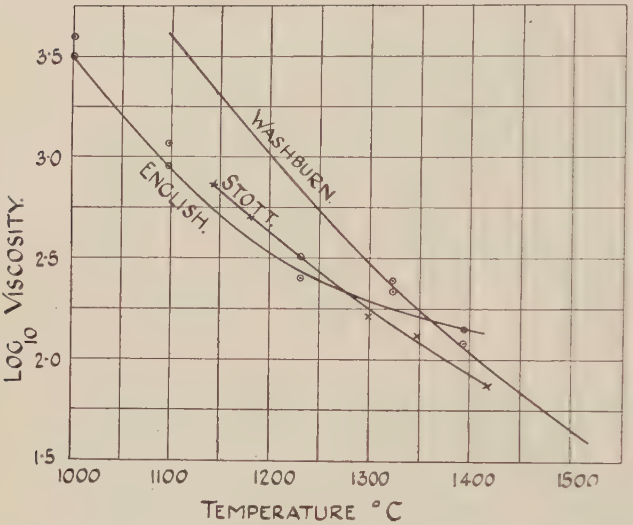


Fig. 1. Comparison of viscosity data obtained by various workers (extracted from paper by Stott, *Journ. Soc. Glass Tech.* **9**, 207 (1925)).

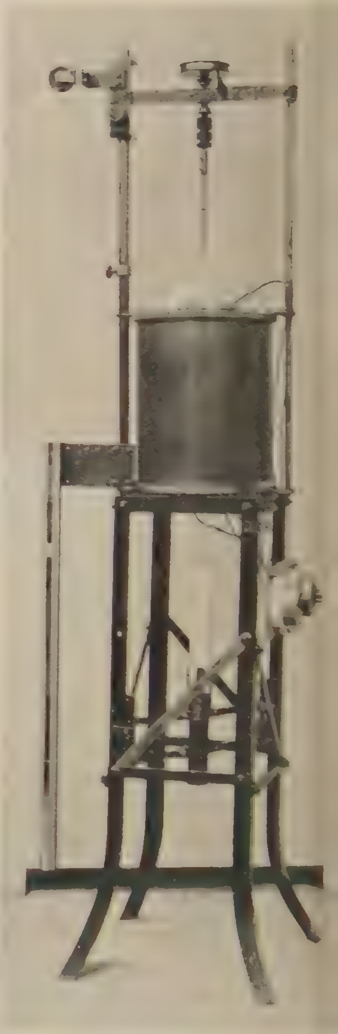


Fig. 2. Rotating cylinder viscomete

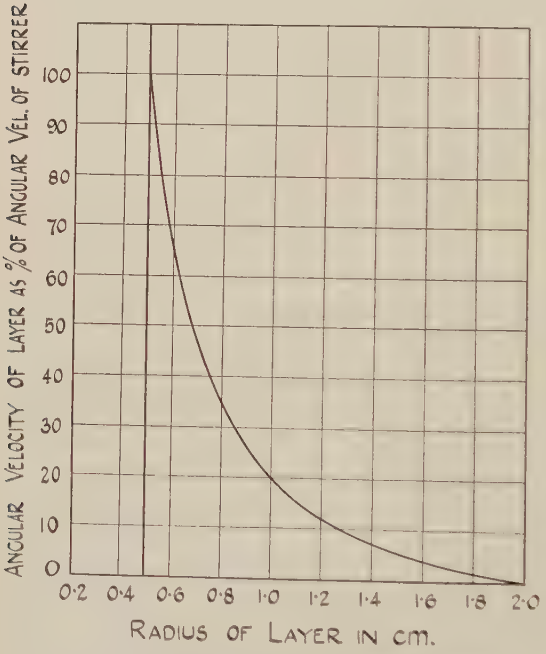


Fig. 3. Diagram showing distribution of angular velocity of the liquid in viscometer.

in a manner which he had previously determined by calibration with liquids of different viscosities.

If a constant factor is used (as suggested by Stott) in calculating the viscosity from Washburn's results, a curve is obtained which has approximately the same slope as that of the other two workers. Later in the paper a constant factor is deduced for Washburn's apparatus based on the authors' experience and the agreement between his results and those of others is improved. A constant factor was employed by English in his measurements. He, however, only calibrated his apparatus at low viscosity values and apparently assumed a constant factor over the whole range.

Whilst the wire method which has been developed so successfully by Stott is ingenious, the calculation of the viscosity from its results involves a knowledge of the surface tension and the authors decided to devote their attention to the rotating cylinder method.

§ 2. DESCRIPTION OF APPARATUS

The general details of the apparatus are shown in Fig. 2. The stirrer has been raised from the furnace and the pillar which supports the pot lowered. For the sake of clearness, the pot has been removed from its position on the pillar and has been placed on the top of the furnace.

The furnace is heated by means of eight silit rods arranged concentrically round the pot. The upper ends of these rods can be seen in the figure. By means of switches it is possible to connect the rods in various series—parallel arrangements; so that a large range of temperature can be covered with the aid of a comparatively small external resistance.

The glass under test is contained in the sillimanite pot which is 4·0 cm. in internal diameter and about 5·5 cm. deep. The pot is kept from revolving by means of a cross, moulded on the bottom of it, which fits into a corresponding recess on the top of the sillimanite pillar. The pillar is clamped in guides and can be raised or lowered as desired.

The stirrer, which is also composed of hard-burnt sillimanite, is made from a bar $12 \times \frac{1}{2} \times \frac{1}{2}$ in., the lower 3 in. of which are accurately ground to 0·97 ± 0·005 cm. The upper portion of the stirrer is roughly ground to fit the mild-steel sleeve and is prevented from turning in it by means of set-screws which engage a groove in the stirrer. The sleeve is clamped in a brass chuck, screwed on to the lower end of a bicycle axle, and can be centred so that the lower end of the stirrer rotates truly about its axis.

The upper end of the axle is attached to a light pulley wheel about 11 cm. diameter. The torque is applied by means of a known weight hung on the end of a fine wire attached to the circumference of the pulley.

By means of set-screws pressing against the circumference of the lower end of the furnace, it is possible to adjust the stirrer so that it is concentric with the pot.

In order to close the top of the furnace as effectively as possible and divert any convection currents away from the main body of the stirrer, a small sillimanite collar is slipped over the stirrer, its height being such that it just clears the under side of the furnace cover. The bottom of the furnace is closed by means of a piece of asbestos cord wrapped around the pillar at the point where it leaves the furnace.

Initially the temperature of the glass was measured by a chromel-alumel thermo-couple arranged in contact with the under side of the pot or its outside edge. However, during the early stages of the measurements it was found that greater accuracy could be obtained by imbedding the couple in the stirrer. Owing to the small diameter of the stirrer, the method adopted is to insert the couple in two holes, moulded throughout the length of the stirrer and connected by a slot at the bottom end. After the insertion of the couple, the slot is cemented up and baked, and the couple is calibrated against a platinum, platinum-rhodium couple which had been previously calibrated against melting points. To allow the stirrer to revolve freely, the thermo-couple is stopped short just outside the top of the stirrer. When it is desired to take a reading, the couple is extended by pieces of the same wires, so that the cold junction is placed in a convenient position. Control of the temperature of the glass is facilitated by the introduction of another couple outside the pot, which is under continuous observation.

The best position for the pot in the furnace was determined experimentally as follows. A pot was filled with glass and the apparatus adjusted in readiness for a test. A fine thermo-couple having a thin silica sheath was then immersed in the glass and the temperature measured at various points, the results being compared with that recorded by the stirrer couple. This was repeated with the pot and stirrer raised or lowered until the most concordant results were obtained. In this position with the furnace temperature at 1000° C., the glass in the neighbourhood of the stirrer was at the same temperature as the stirrer and the glass remote from it differed on the average by 2°, the maximum difference at the ends of the pot being 5°. The differences are less at the lower temperatures. As will be seen later, the rate of change of the angular velocity of the glass increases from the walls to the stirrer. If, therefore, the temperature distribution is not rigidly constant, it is better to measure the temperature at the stirrer rather than at the walls of the pot.

§3. DISCUSSION OF ERRORS

Before the calibration of the apparatus was commenced, the effect of errors in measured quantities on the precision of the measurements was determined.

The factors considered were:

(1) Measurement of temperature.
(2) Diameter of pot.
(3) Diameter of stirrer.
(4) Height of liquid in pot.
(5) Friction of rotating system.
(6) Depth of immersion of stirrer.
(7) Eccentricity of stirrer.
(8) Deviation of axis of rotation from axis of stirrer.
(9) Load.
(10) Speed of rotation.

(1) *Temperature measurement.* In the case of concentric cylinders, where the outer cylinder is stationary, it can be deduced theoretically that, neglecting friction and end corrections,

$$\eta = K\,M/\phi_o$$

$$\text{where } K = (gR/8\pi^2 l)\,(1/r_i^2 - 1/r_o^2) \qquad \ldots\ldots(1).$$

η is the viscosity in c.g.s. units,
M the load on the wire,
R the radius of the pulley,
l the length of the cylinders,
r_o the radius of the outside cylinder,
r_i the radius of the inside cylinder, and
ϕ_o the revolutions per second of the inner cylinder.

It follows that

$$\phi = (MgR/8\pi^2 l\eta)\,(1/r^2 - 1/r_o^2) \qquad \ldots\ldots(2)$$

where ϕ is the angular velocity at radius r.

Fig. 3 gives the velocity of the liquid at any point between the cylinders as a percentage of that of the inner cylinder, calculated by means of Equation (2), for cylinders having radii approximately equal to those of the pot and stirrer respectively. It is seen that, in this case, the velocity of the liquid at a distance of 0·1 cm. from the stirrer is about 32 per cent. less than that of the stirrer, whereas the change in velocity over a corresponding distance adjacent to the walls of the pot is less than 1 per cent.

From this it is clear that, for a given change in η, the change produced in ϕ_o is much greater for small values of r than for large. This point can also be demonstrated by differentiating Equation (2) with respect to r. For accurate working, therefore, it is more important to measure correctly the temperature of the layers adjacent to the stirrer than to measure correctly the mean temperature of the glass wherever the temperature is not rigidly constant.

The temperature determined by the couple in the stirrer is considered to be within ± 2° of the true temperature at 1000° C.

(2) *Diameter of pot.* For a reason similar to that discussed in the previous section, small variations of the order of 0·05 cm. in the diameter of the pot do not appreciably affect the viscosity measurements.

(3) *Diameter of stirrer.* An examination of the curve given in Fig. 3 shows that an error of 0·005 cm. in the diameter of the stirrers (which represents the limit of accuracy of the stirrers) produces an error of about 1 per cent. in the measurements.

(4) *Height of liquid in pot.* Similarly Equation (1) shows that an error of 0·02 cm. in the measurement of the height of the liquid in the pot introduces an error of about $\frac{1}{2}$ per cent. into the viscosity measurements. As Equation (1) does not take into account the end effects, it is probable that the actual error produced by the above difference in height is somewhat less than this amount. (Since the apparatus is calibrated against liquids of known absolute viscosity, the actual end correction does not matter.)

(5) *Friction of rotating system.* This was determined over a wide range of velocities with the stirrer rotating in air. It was found that whilst the friction varied from day to day, the value of the load equivalent to the friction lay between 1·5 to 1·8 gm. weight and there was no appreciable variation with speed.

(6), (7) and (8). *Errors due to changes in the relative positions of stirrer and pot.* To determine the magnitude of the errors due to causes (6), (7) and (8), a series of tests was made with Lyle's golden syrup. For these tests the sillimanite stirrer and pot were replaced by a brass tube and pot respectively, and in order to improve the accuracy of the temperature measurements, they were raised out of the furnace and surrounded by a water jacket. The temperature was measured by a thermocouple placed inside the stirrer, which contained a little glycerine to improve the thermal contact. The temperature was maintained constant to within 0·1° C.

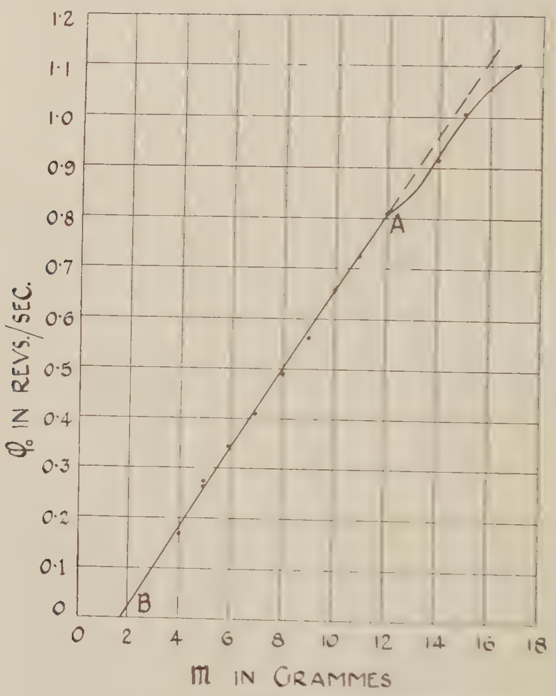


Fig. 4. Diagram showing relation between angular velocity of stirrer and applied load.

With the stirrer raised, the pot was filled with syrup to a depth of 5·0 cm. The stirrer was next lowered to the bottom of the pot and then raised 0·5 cm. Before readings were taken one complete revolution was allowed to ensure of the stirrer attaining a uniform velocity. This was found to give sufficient time for the stirrer to reach approximately uniform motion.

In making the measurements the time of three complete revolutions was taken for various loads and the revolutions per second calculated. The results of a typical test are shown in Fig. 4.

When the angular velocity of the stirrer exceeded a certain definite value turbulent motion set in, as is seen by the departure from the linear relation between M and ϕ_0 at A. It is of interest to note also that the intercept on the load axis is 1·7 gm. weight corresponding to the friction as determined in air. In all viscosity determinations the slope of the straight portion AB corresponding to purely viscous flow was used in the calculations. Experiments were made for a number of relative positions of pot, stirrer and axis of rotation. The results are given in Table 2, where errors in viscosity due to various errors in adjustment are given for these experiments.

Table 2. Errors in viscosity due to variations in adjustment of apparatus

Adjustment	% change in M/revs. per sec. due to 0·1 cm. variation in adjustment	Accuracy of adjustment in cm.	% error in final result due to error of col. 3.
(1)	(2)	(3)	(4)
Distance of stirrer from bottom of pot	2·6	0·02	0·5
Eccentricity of stirrer and pot	0·9	0·02	0·2
Eccentricity of stirrer from axis of rotation	1·3	0·015	0·2

(9) *Load.* The load could be determined to as high an accuracy as desired.

(10) *Speed of rotation.* At the higher speeds the accuracy of an individual measurement was about 1 per cent., but to improve this more repeat observations were made at the higher than at the lower speeds.

§ 4. CALIBRATION OF APPARATUS

For the calibration of the apparatus at low viscosities (about 10^3 c.g.s. units) Lyle's golden syrup was employed. To determine the viscosity of the syrup a falling sphere viscometer of the following dimensions was employed:

Length of tube	40·3 cm.
Radius of tube	1·125 cm.
Radius of sphere	0·0793 cm. (1/16 in. Hoffman ball.)

The viscosity was calculated from the rate of fall of the sphere through the central portion of the column by means of the Ladenburg formula (9), viz.:

$$9\eta V(1+2\cdot4x)(1+3\cdot3\,r/h)=2gr^2(s-\sigma),$$

where V is the velocity of sphere,
η the viscosity,
x the radius of the sphere (r) divided by the radius of the vessel,
h the height of liquid in vessel,
s the density of the sphere, and
σ the density of the liquid.

In calibrating the rotating cylinder apparatus with the syrup, the following procedure was adopted. The viscosity of a portion of the syrup was first measured over a range of a few degrees, at a suitable temperature, by means of the falling sphere viscometer. The centre portion of the column of syrup was then transferred to the pot and a series of measurements of load and revolutions per second was taken in the rotating cylinder apparatus as soon afterwards as the steadying up of the temperature of the syrup would allow. To increase the accuracy of the determination of ϕ_0 (the revolutions per second) three revolutions were allowed to pass, the time for the twelve subsequent revolutions was measured, and this measurement was repeated on several occasions. During both of the determinations the temperature of the syrup was kept steady to within 0·1° C. (approximately). The calibration factor (K in Equation (1)) for the apparatus was then determined from the viscosity of the syrup and the slope of the load revolutions-per-second curve.

Five independent calibrations were made, a fresh portion of syrup being used each time. To eliminate any possibility of error due to variation of the viscosity of the syrup owing either to time or to lack of homogeneity, a separate determination of the viscosity by the falling sphere method was made for each calibration.

The results of the five calibrations are shown in Table 3.

Table 3. Calibration factor determined with syrup

Viscosity c.g.s. units	K	Mean K	% variation from mean
523·6	52·2	53·4	− 2·3
203·0	54·6		+ 2·2
264·9	53·7		+ 0·64
478·6	53·2		− 0·32
337·3	53·3		− 0·13

For calibrating the apparatus at high viscosity values, pitch was employed. As it was not convenient to use the falling sphere viscometer owing to the high viscosity necessitating long periods of time, and the opacity of the pitch requiring the use of X-rays, it was decided to determine its viscosity by means of torsion.

Rods about 20 cm. long by 1·3 cm. in diameter were made by rolling the pitch between two flat boards, in a manner similar to that described by Trouton and Andrews (10), and square tapered ends were pressed on to them by means of the brass cups (see Fig. 5).

The lower brass cup was clamped to the top of the furnace to prevent it from rotating, whilst the upper cup was mounted in the chuck of the stirring gear. A bath containing a solution of calcium chloride was fixed around the pitch rod to prevent it thinning down at the top owing to viscous flow under gravity. By means of an electric heater the bath could be kept at any desired temperature.

To eliminate any errors due to twisting of the ends of the rod, the following procedure was adopted. In essentials it is similar to that used by Stott (5) in his low-temperature viscosity measurements. A fine line was made down one side of the rod and the diameter of the rod was measured in several places. The rod was then mounted in place and the temperature steadied. After the temperature had been steady for about 20 minutes a set of readings of time and distance through which the weight had fallen was recorded for a given load. A typical set of observations is shown in Fig. 6. (As the circumference of the pulley wheel is 34·5 cm., one revolution of the stirrer corresponds to 34·5 cm. fall of the weight.) At the end of the test the mean distance between consecutive turns of the helix was measured by means of a pair of sliding calipers. The rod was then taken out and remeasured. The rod was replaced in the apparatus, the pitch of the helix was measured and a second test was carried out with a different load. As before, after a series of readings of time and distance traversed by the weight had been taken, the new mean pitch of the helix was measured. In this manner it was found possible to utilise the same rod for three or four tests. The minimum pitch used was 2·5 cm. which could be measured to within 0·025 cm., i.e. 1 per cent.

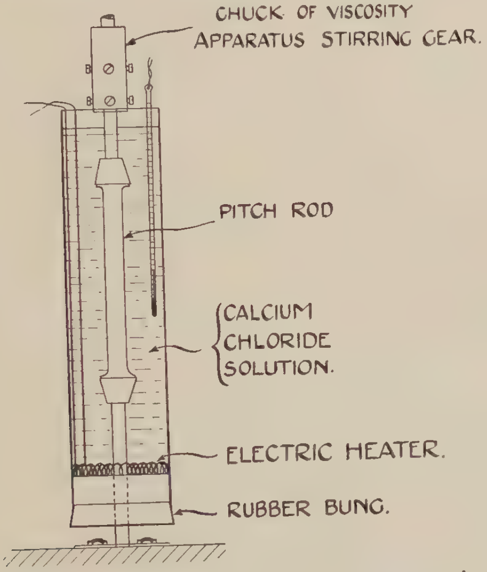

CHUCK OF VISCOSITY APPARATUS STIRRING GEAR.
PITCH ROD
CALCIUM CHLORIDE SOLUTION.
ELECTRIC HEATER.
RUBBER BUNG.

Fig. 5. Supplementary apparatus for measuring viscosity of pitch by torsion.

It can be shown theoretically that

$$\eta = 2MgR/\pi\omega r^4 = (2Rg/\pi r^4)\, M/\omega \qquad \text{......(3)},$$

where M is the load,

R the radius of the pulley,

r the radius of the pitch rod,

ω the angular velocity of twist of rod per unit length, viz. $2\pi/pt_c$,

p the mean pitch of helix, and

t_c the time of test corrected for plastic flow.

The value of t_c is determined as follows. Referring to Fig. 6,

$$t_c = OD \times AD/AB = t \times AD/AB.$$

The mean pitch corresponding to any one test was calculated from the initial and final pitches by means of the equation

$$p = p_o p_l/(p_o - p_l)$$

where

p_o is the initial pitch of the helix and
p_l the final pitch of the helix.

From the measurements of the pitch of the helix and from the time-scale-reading curves for various loads, similar to Fig. 6, the straight lines in Fig. 7 showing the change of ω with M have been calculated.

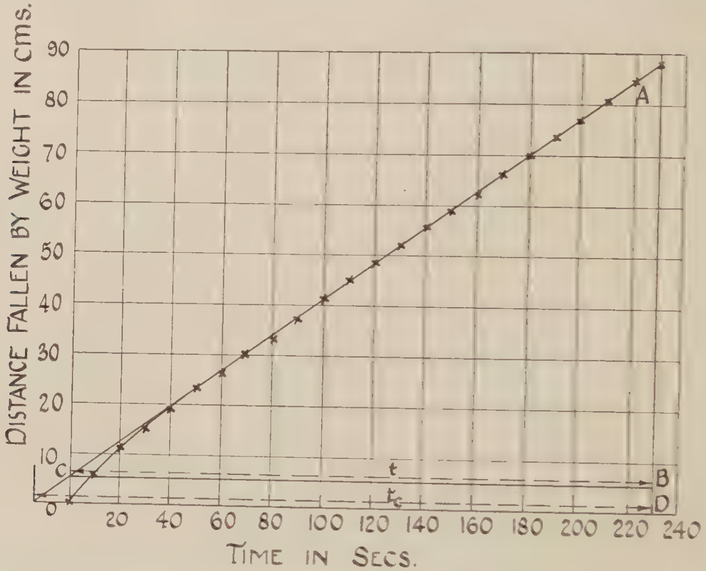


Fig. 6. Diagram showing relation between the twist and time for pitch rods subjected to torsion.

Substituting the values for the slope of these lines in Equation (3), we obtain for the viscosity of the pitch the results shown in Table 4. These results have been plotted in Fig. 8.

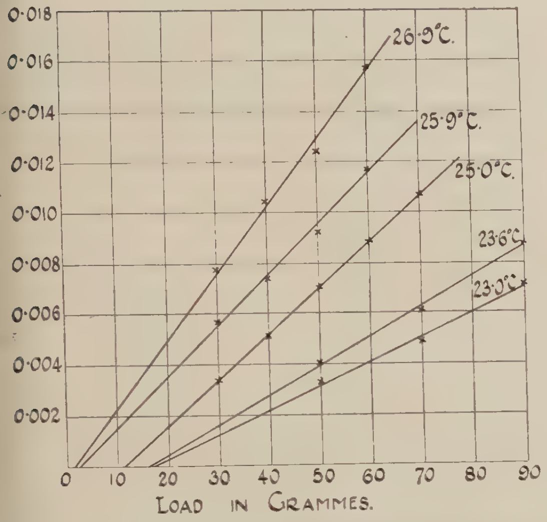
Table 4. Viscosity of pitch

Temp. ° C.	Viscosity in c.g.s. units	$\log_{10}$ viscosity
23·0	$1{\cdot}906 \times 10^8$	8·281
23·6	$1{\cdot}557 \times 10^8$	8·193
25·0	$0{\cdot}987 \times 10^8$	7·994
25·9	$0{\cdot}904 \times 10^8$	7·954
26·9	$0{\cdot}683 \times 10^8$	7·834

Half of the rods used in the torsion measurements were then melted into the pot of the rotating cylinder viscometer, only sufficient heat to let the pitch gradually settle down in the pot being used. After the temperature had been steady for about

30 minutes, the speed of rotation of the stirrer was determined for loads of 200, 300, 500, 1000, 1500 and 2000 gm. weight. The results are shown in Fig. 9.

Referring to Fig. 8 and Equation (1), we obtain $K = 52{\cdot}4$.



g. 7. Diagram showing the relation between twist and ad for pitch rods under torsion at various temperatures.

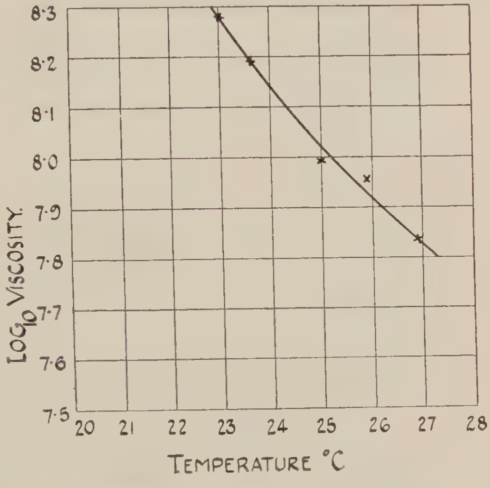


Fig. 8. Diagram showing viscosity-temperature relation for pitch.

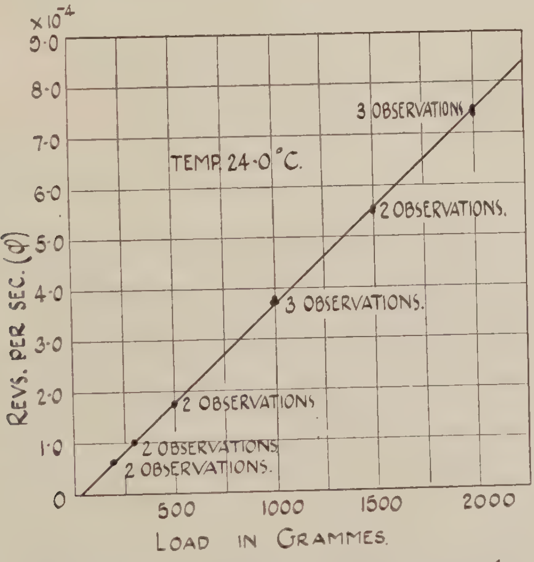


Fig. 9. Diagram showing relation between angular velocity and load for pitch.

A repeat test made with the remaining half of the rods gave $K = 51{\cdot}5$. The mean result is 52·0, which is 3 per cent. lower than the constant calculated from experiments with syrup.

As the determination of the calibration factor, when pitch having a viscosity of about 10^8 c.g.s. units is used, agrees with the value obtained with syrup at a viscosity of 10^3 c.g.s. units, within the limits of accuracy of the present measurements, it was felt that determinations of the calibration factor at intermediate viscosities was unnecessary.

Further, the calibration constant adopted for subsequent work is 53·0, a value approximating nearer to that obtained when using syrup. This value, the authors feel, is justified in view of the greater inherent difficulty in determining the viscosity of the pitch.

§ 5. DISCUSSION OF RESULTS

From the foregoing results it appears that, contrary to Washburn's experience, the calibration factor for a rotating cylinder viscometer is independent of the viscosity, over the range 10^3 to 10^8 c.g.s. units at any rate. As Washburn's calibration factor was the result of a direct calibration over the whole range of viscosity covered by his measurements, it is desirable to seek for an explanation of the large variation he obtained in the value of his factor with viscosity.

A possible explanation was suggested to the authors as the result of some viscosity measurements made on a sodium silicate solution. When they commenced the present measurements they had intended to use sodium silicate as a calibrating medium in place of syrup owing to its higher viscosity. It was found, however, impossible in this case to obtain concordant figures for the calibration factor of the rotating cylinder viscometer, the results of four successive calibrations being

63·0, 64·8, 67·1, 84·0,

a variation of over 30 per cent. The results obtained by the falling sphere viscometer did not show any marked change in the viscosity of the sodium silicate. The large changes above noted were attributed to the development of a skin on the sodium silicate.

When the stirrer was immersed into the pot, it would carry this skin part of the way down with it, a portion only of the stirrer piercing the skin. The effect of this would be to create a thin air film round the upper portion of the stirrer and thus reduce its effective length. This would cause the stirrer to revolve faster, for a given torque, than it would if its whole length were in contact with the liquid, resulting in a high value for the calibration factor. The skin was found to be more pronounced and more troublesome as the calibration work proceeded, and probably this accounted for the ascending magnitude of the factor.

The calibration curve obtained by Washburn for his apparatus is reproduced in Fig. 10, where 1, 2, 3, 4, 5, 6 refer to his various calibration glasses. Glasses 1, 2, 3, 4 were made from confectioner's glucose with various percentages of water, whilst 5 and 6 had a small percentage of dextrose added. It is stated that glasses 3 and 4 both developed a skin very rapidly; this was very tough in the case of 4. Although it is not stated, it is very probable that 5 and 6 also had troublesome skins on them.

As the values of the viscosity of the glass determined by at least two different methods agree reasonably amongst themselves, it is probable that there is no serious error in them. The authors' experience with sodium silicate suggests that skins on Washburn's glasses produced errors similar to those mentioned above. This suggested conclusion is supported by the fact that glass 4, which Washburn states to have had a very tough skin, gave a particularly high value for the calibration factor. The authors have accordingly drawn the best straight line, yielding a constant calibration factor, through the values obtained for glasses 1 and 2 which were apparently the only ones practically free from a skin. This is shown as a broken line in Fig. 10, and the authors have used it in adjusting Washburn's results before comparing them with their own measurements and those of the other workers.

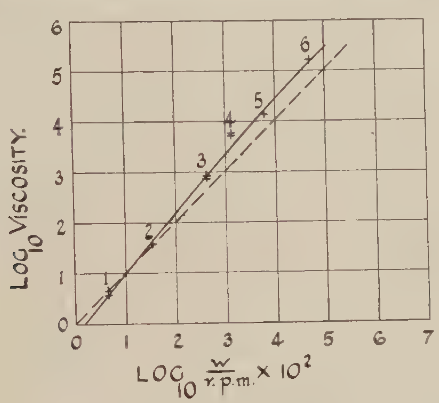


Fig. 10. Diagram showing Washburn's calibration data for his viscometer.

§ 6. MEASUREMENT OF THE VISCOSITY OF GLASS

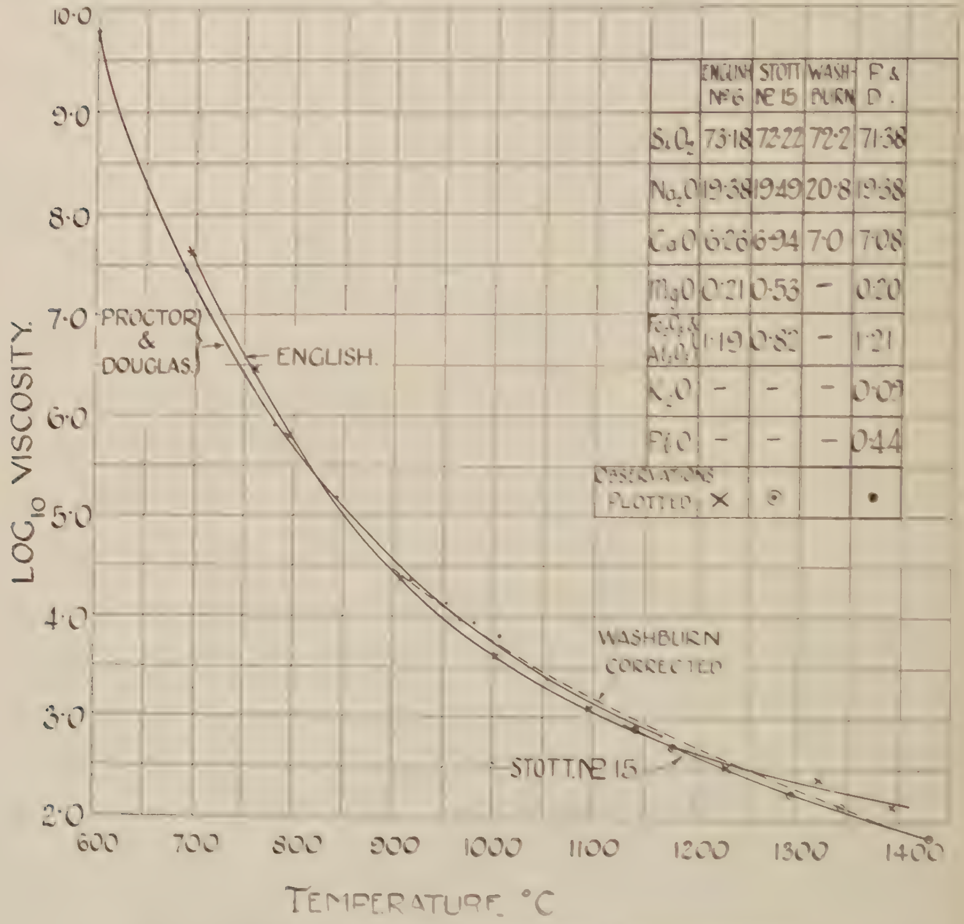
In conclusion, the authors give the results of viscosity measurements on a glass (*C*) having a composition similar to those used by others (see Table 5), and following the lines of the previous discussion they attempt to compare the observations with those already published.

Table 5. Viscosity data for Author's glasses

Glass *A*		Glass *B*		Glass *C*	
Temp. ° C.	Log_{10} viscosity	Temp. ° C.	Log_{10} viscosity	Temp. ° C.	Log_{10} viscosity
577	8·820	755	5·924	600	9·812
661	7·337	810	5·339	692	7·444
755	5·995	834	5·133	780	5·906
854	4·977	890	4·689	844	5·182
927	4·389	927	4·519	920	4·345
1048	3·616	932	4·457	953	4·131
1152	3·237	1034	3·725	968	3·965
		1113	3·312	983	3·933
		1182	2·978	1008	3·789
				1055	3·368
				1168	2·822

The accuracy of their determinations for glass is not quite as high as that for the syrup owing to increased difficulty in adjusting the apparatus at high temperatures. It is considered, however, that the errors in the viscosity measurements due to all sources are less than about 6 per cent. at 1200° C. and 10 per cent. at 700° C.

It is interesting to note that the authors experienced a reduction in the accuracy of their results round about 950–1000° C. similar to those experienced by Stott. They hope to investigate this effect further in future work.



	ENGLISH Nº 6	STOTT Nº 15	WASHBURN	F & D.
SiO_2	73·18	72·22	72·2	71·38
Na_2O	19·38	19·49	20·8	19·38
CaO	6·26	6·94	7·0	7·08
MgO	0·21	0·53	–	0·20
Fe_2O_3 & Al_2O_3	1·19	0·82	–	1·21
K_2O	–	–	–	0·09
TiO	–	–	–	0·44
OBSERVATIONS PLOTTED	×	⊙		•

Fig. 11. Authors' comparison of viscosity data by different workers.

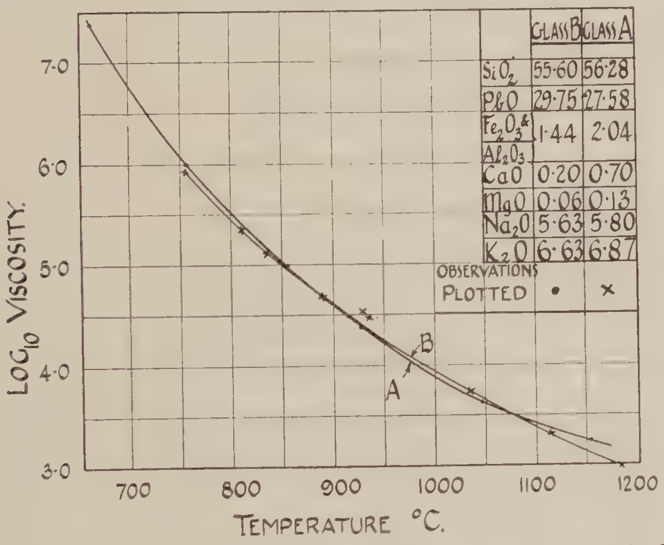
In Fig. 11 have been plotted the viscosity results of English, Stott, Washburn, and the authors on glasses of the composition shown in Table 6.

As already noted in the introduction to this paper, the glasses used by Washburn were made by mixing three known glasses in various proportions, the compositions being calculated from analyses of the three parent glasses. In the calculation the impurities were apparently neglected. From an examination of analyses of two of his glasses it would appear that his calculated values for SiO_2 and CaO

Table 6. Analyses of glasses compared in Fig. 11

	English, No. 6	Stott, N.P.L. 15	Washburn (from isokoms)	Proctor and Douglas
SiO_2	73·18	72·22	72·2	71·38
Na_2O	19·38	19·49	20·8	19·38
CaO	6·26	6·94	7·0	7·08
MgO	0·21	0·53	—	0·20
Fe_2O_3 and Al_2O_3	1·19	0·82	—	1·21
K_2O	—	—	—	0·09
PbO	—	—	—	0·44

are much closer to the actual values than that for Na_2O. In view of this, it was decided to fix his glass from a consideration of the percentages of SiO_2 and CaO only. As Washburn's isokoms only make a small angle with the line of constant SiO_2 in his triangular diagrams, for a glass of the above composition, small differences in Na_2O and CaO do not appreciably affect his results. It will be seen that the correction applied to Washburn's results brings them within 25 per cent. of Stott's values over the whole temperature range, and the results obtained by the authors are also practically in agreement with Washburn's, indicating that his glass approximated quite closely to those used by Stott and the authors and that the figure for alkali content probably includes the minor constituents.



	GLASS B	GLASS A
SiO_2	55·60	56·28
PbO	29·75	27·58
Fe_2O_3 & Al_2O_3	1·44	2·04
CaO	0·20	0·70
MgO	0·06	0·13
Na_2O	5·63	5·80
K_2O	6·63	6·87
OBSERVATIONS PLOTTED	•	×

Fig. 12. Diagram showing temperature viscosity curves for two lead glasses differing slightly in composition.

In considering English's data, the authors desire to point out that the glass used by him differs quite appreciably from that used by them and has also the lowest lime content of any of the glasses. Stott criticised English's data for the higher temperatures. In a short note written by English as a contribution to a discussion on viscosity, he makes reference to this and suggests a value of 10^3 as a lower limit for his apparatus, in view of small errors in his frictional constant appreciably affecting the results. The authors agree that it is possible for errors from this cause, together with errors due to the inertia of the stirring apparatus, to affect the values of viscosity in this range.

However, the differences in composition cannot be ignored, and in order to emphasise the effect of small changes in composition the compositions and viscosity data for two lead glasses are given in Fig. 12 (and Table 5), whence it will be seen that the differences between the viscosity temperature curves for these glasses are similar in character to the differences between the curves given by English and the present authors.

It appears, therefore, that all the published data (including Washburn's as corrected by the authors) are in reasonable agreement when allowance is made for the variations in composition.

§ 7. ACKNOWLEDGMENT

The authors wish to thank Mr A. L. Robotham for his assistance in a portion of the investigation.

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DISCUSSION

Mr C. C. **Paterson**: As Director of the Laboratories I should like to offer a hearty welcome to the members of the Physical Society and the Society of Glass Technology.

Mr Proctor has given an account of experiments showing that it is possible to measure, fairly easily and in absolute units, the viscosity of glass over the range at which founding and working takes place. I should like to emphasise how important it is to know and control the viscosity of glass under modern manufacturing conditions. Automatic machine production of glass articles means working the material at as high a speed as possible. The flow of the glass under these conditions must be uniform for the temperature fixed for the operation, otherwise the processes will be thrown out of gear. I would invite members to study this factor in the bulb-making machines in the glass works you will be visiting, and also in the lamp-making operations.

Mr Dudding has asked me, on behalf of my colleagues here, to invite those members of the Society of Glass Technology who control similar factory operations and who have accurate repeat analyses of their glass, to send us samples which we can test in this viscosity apparatus over the working range. We should be pleased to give them the results, and we think that a comparison, under identical conditions, of a number of glasses of different but well established composition, will be of value to all of us who are seeking to prescribe the best conditions for industrial glass manipulation.

Dr S. ENGLISH: I have been very interested in the paper for both personal and technical reasons. Perhaps I may be permitted to mention the personal reasons first. In 1924 there appeared almost simultaneously two fairly comprehensive papers on the viscosity of glass up to and in some cases beyond 1400° C.; one was by myself and the other by Prof. Washburn and Mr Shelton. Unfortunately, when dealing with glasses of somewhat similar composition, there was not that concordance in the results that could have been desired. At intervals, since that time, these two sets of data have been reviewed by various workers who seem to have emphasised whatever divergence there was, with the result that confidence in both pieces of work may have been undermined. I am therefore pleased that the authors have so thoroughly investigated the many problems in this very difficult measurement, and that as a result of their work they have been able to confirm my own results and also discover the cause for the divergence between the data given in my paper of 1924 (part II) and those given by Washburn and Shelton. Regarding the curves reproduced in Fig. 1, I thought that I had been able to explain the difference between the curves marked "English" and "Stott"* and to show that this difference was accounted for by difference in composition, but I am glad to have the corroboration of Messrs Proctor and Douglas in this matter also.

Turning to the technical side, as one who knows the difficulties to be overcome in this particular branch of research, I should like to congratulate the authors on the thoroughness with which they have investigated sources of error, and the care they have taken to ensure accuracy. I have, however, one criticism to make. I consider that, in spite of its cost, the use of a platinum iridium sheath as the inner rotating cylinder is well worth while when dealing with non-lead glasses. Its diameter and surface remain constant for every determination, and its introduction into the molten glass does not give rise to bubbles such as occur whenever a new clay, or sillimanite stirrer is used. A new stirrer of this type is necessary for each determination.

There is one question not mentioned by Mr Proctor in the presentation of this paper which I should like to ask him. In May of last year†, when reviewing

* *Journ. Soc. Glass Tech.* **10**, 32 (1926).

† *Ibid.* **12**, 106 (1928).

critically the methods of measuring the viscosity of glass, I suggested that, owing to frictional corrections becoming relatively large when the viscosity of the glass was small, this rotating cylinder method is liable to lose its accuracy when the viscosity of the glass is less than 10^3 c.g.s. units. I should be glad to hear whether the authors agree with this suggested useful limit for viscosity apparatus of this type.

Mr V. H. STOTT: I wish to congratulate the authors on their very interesting work achieved in the face of considerable experimental difficulties. Unfortunately, I have only just received a copy of the paper, but it has occurred to me that there are two main objects in measuring the viscosity of glass. In the first place, an absolute measurement of viscosity may be desired, or, on the other hand, it may be wished merely to have a sensitive means of checking the variations of viscosity for works control. For the former purpose an apparatus on the lines of that used by the authors is probably the most convenient. It has, however, the disadvantage of permitting a gradual contamination of the glass owing to the solution of the refractory materials in contact with it. Perhaps the authors could tell me whether they experienced trouble of this kind.

Having in mind the second purpose, we have used, in the National Physical Laboratory, an apparatus based upon a phenomenon investigated by the staff of the General Electric Company. The apparatus is easy to use, very sensitive, and gives closely repeatable results. As the glass is in contact only with an alloy of platinum, it is possible to work on a sample of glass for months at a time, and perform experiments on the effects of heat treatment of the glass which would be impossible with an apparatus using ordinary refractory materials. In view of the remarks of Mr Paterson, this apparatus would seem to be particularly suitable for his requirements.

In conclusion, I should like again to congratulate the authors for having introduced some measure of co-ordination between the results of previous workers. This is very important.

Prof. W. E. S. TURNER: I should like to express my thanks to Messrs Proctor and Douglas for their work on a subject which has proved to be of great interest and first class importance in the past five or six years. Although their work seems to me to have been excellent, the authors may feel still more assured if I remark that recently I was privileged in America to see two papers by Mr Lillie covering much the same ground as the paper by Messrs Proctor and Douglas and reaching very closely similar conclusions, namely, that the measurements of Washburn and Shelton of the viscosity of different glasses were in themselves made correctly, and that any errors in the final results are to be traced to the calibration factor, and finally that the measurements of English are reasonably well substantiated.

AUTHORS' reply: In reply to Dr English: we agree with him in fixing a viscosity of 1000 c.g.s. units as an approximate lower limit for an apparatus having similar dimensions to our own, owing to frictional errors seriously reducing the accuracy of the measurements at lower viscosities. However, by using a stirrer and pot of larger diameter this limit could probably be considerably lowered. We should like to thank Dr English for drawing our attention, just prior to the meeting, to a further paper of his which we regret to have overlooked. In this he discusses the differences between his results and those of Mr Stott at the higher temperatures.

In answer to Mr Stott: no visible corrosion of the pot and stirrer could be detected after a test. A new pot and stirrer were used for each glass. As we intended to include lead glasses in the measurements we felt that it was not advisable to use a platinum stirrer and pot, owing to the interaction of lead glass and platinum.

We considered the wire method, but decided in favour of a rotating cylinder apparatus. The wire method is open to two criticisms. Firstly, the calculation of the viscosity from the experimental data involves an accurate knowledge of the surface tension of the glass over the whole range of temperature. Secondly, the glass carried out of the pot by the wire is mainly drawn from the surface layers, and any volatilisation of the glass or incipient surface devitrification would seriously affect the accuracy of viscosity measurements.

THE BAND SPECTRUM OF LANTHANUM MONOXIDE

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ABSTRACT. The spectrum has been observed from λ 8700 to λ 2850, and the band-heads (most of them not hitherto recorded) arranged into several systems. While the work was in progress Auerbach[*] gave high dispersion data for some of the new infra-red heads, and Mecke[†] briefly reported the analysis of seven systems, having 0, 0 bands at (1) λ 4372; (2) λ 4418; (3) λ 5600; (4) λ 7380; (5) λ 7404; (6) λ 7877; and (7) λ 7910. Mecke concluded that (*a*) systems 3, 5 and 7 have a common final state; (*b*) so have systems 1 and 2; and (*c*) the initial states for 1 and 2 appear to be the final states for 4 and 6 respectively.

The author's analysis of 2 differs from Mecke's, the 1, 2 band in the former being the 0, 1 band in the latter. Hence, while Mecke's conclusion (*a*) is approximately confirmed, (*c*) becomes untenable if (*b*) is true, as it probably is. If systems 1 and 2 have states in common with 4 and 6 respectively, they must be the final states in each case. Systems 4 and 6 resemble one another in appearance and in initial and final vibrational frequencies, but probably have no state in common. They may represent the *R* heads of two systems of which 5 and 7 respectively are strong *Q* heads; the pair of systems ($\Delta\nu_e = 864$ cm.$^{-1}$) having a common final state and corresponding to the infra-red ${}^2P \rightarrow {}^2S$ doublet of *Cs* ($\Delta\,{}^2P = 554$ cm.$^{-1}$); but there appears to be evidence against this interpretation. Some ultra-violet bands, λ 3710 – λ 3457, degraded towards shorter wave-lengths, i.e. opposite to those of systems 1 . . . 7, have been measured. Eight of these appear to belong to an incompletely traced eighth system due to a transition from the final state of one or more of the above systems, e.g. 3, 5, 7, to the initial state of another, e.g. 1 or 2.

Appendix. A brief note is given on the general theory of electronic band spectra of diatomic molecules.

§ 1. INTRODUCTORY

In the lanthanum section in Volume **5** of Kayser's *Handbuch*[‡] are collected data for five groups of bands in the visible region, which have since been assigned to lanthanum oxide[§]. The bands all degrade towards the red, the most refrangible heads of the groups being at $\lambda\lambda$ 4372, 4418, 5380, 5600 and 5863 A. respectively. The first two groups, for which further data have been given by F. Exner and E. Haschek[||] and by J. Ôkubo[¶], are similar to one another in intensity and in spacing, and appear on first inspection to be neighbouring sequences of a common band-system; brief examination of the data shows that they are more probably the prominent sequences of two closely related band-systems, which will be called systems 1 and 2, for reasons appearing presently. The remaining three groups are easily recognisable as fragments of three neighbouring sequences (with $n'' - n' = -1$, 0 and $+1$ respectively) of another band-system, 3.

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[*] *Naturwissenschaften*, February 1, 1929.

[†] *Ibid.*

[‡] *Handbuch der Spectroscopie*, **5**, 667 (1910).

[§] A. Hagenbach and H. Konen, *Atlas of Emission Spectra*, A. S. King's English Edition (1905), p. 30 and charts XIII (strip 127) and XIV (strip 137). Lanthanum sulphate in carbon arc in air.

[||] *Die Spectren der Elemente bei Normalem Druck*, **2**, 117 (1911).

[¶] *Tôhoku Univ. Sci. Reports*, **11**, 95 (1922).

In the *Tabelle der Bandenspectra*[*] Kayser gives approximate wave-lengths for the band-heads in two further lanthanum groups in the red, degrading, like the former bands, in the long-wave direction, and beginning at λ 6995 and λ 7380 respectively. These groups appear at first sight to be two sequences of one system of double headed bands, but closer investigation shows that in each group alternate bands belong to two separate systems, which will be called 4 and 5.

In October and November 1928 the author photographed and measured a large number of new bands of all the above systems, except system 1, and also two new groups of bands in the near infra-red, somewhat resembling Kayser's red groups and degrading towards longer wave-lengths from λ 7877 and λ 8453 respectively. Some of these infra-red bands fell naturally into one of the systems already mentioned, namely ,system 5; others were arranged in a new system, referred to below as system 7; and the remainder formed fragments of three sequences (one quite definite and two somewhat uncertain) which the author failed to connect either with one another or with the other band-systems. From the conditions of development of the red and infra-red bands it was clear that they belonged to the same spectrum as the earlier known bands in the visible region, and were due to an oxide, which the simplicity of the systems indicates as diatomic, i.e. LaO.

At this stage, when systems 2, 3, 4, 5, and 7 had been recognised and analysed, the investigation had to be put aside for four months on account of pressure of other work. On resumption, some higher dispersion data were obtained for the red and infra-red band-heads, and a description of the work for publication was begun, when the writer's attention was drawn[†] to two letters which had appeared in the meantime briefly recording an investigation of the same spectrum at Bonn. In the first letter Frl. H. Auerbach[‡] gives very precise grating data of most of the band-heads of the two new groups in the infra-red, and in the second Dr R. Mecke[§] summarises a vibrational analysis resulting in seven band-systems, the heads of which are given approximately by formulae of the usual type[||], namely,

$$\nu_{\text{head}} = (\nu_e + \kappa) + [a'(n' + \tfrac{1}{2}) - b'(n' + \tfrac{1}{2})^2] - [a''(n'' + \tfrac{1}{2}) - b''(n'' + \tfrac{1}{2})^2],$$

in which the coefficients have the values shown in Table 1. The numbers 1 to 7 adopted throughout the present paper to designate the systems are those used by Mecke.

From a study of the vibrational energy coefficients for the electronic states involved in the seven systems, Mecke concludes that (*a*) systems 3, 5 and 7 have a common final state; (*b*) systems 1 and 2 have a common final state; (*c*) the initial state for system 1 appears to be the final for system 4; (*d*) the initial state for system 2 appears to be the final for system 6. Dr Mecke finally notes that no ultra-violet system has yet been observed which combines one of the systems 3, 5 and 7 with one of the systems 1, 2, 4 and 6.

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[*] *Handbuch der Spectroscopie*, **6**, 1036 (1912).

[†] By Prof. R. S. Mulliken in a letter received April 1.

[‡] *Die Naturwissenschaften*, **17**, 84 (February 1, 1929).

[§] *Ibid.* p. 86.

[||] Actually Dr Mecke's formulae were given in the form indicated by the earlier quantum theory, and have here been converted into the new mechanics form.

Table 1. System-origins and vibrational frequency coefficients (Mecke)

System	$(\nu_e + \kappa)$, ÷ System-origin, ν_e	Initial state		Final state	
		a'	b'	a''	b''
1	22874·9	806·3	1·8	826·5	2·0
2*	22638·4	801·8	1·8	826·5	2·0*
3	17886·1	732·85	2·15	816·3	2·20
4	13575·5	750·1	1·96	807·0	1·87
5	13532·0	760·6	2·2	816·6	2·18
6	12719·6	745·5	1·8	801·8	1·8
7	12665·7	762·0	2·2	816·6	2·18

As has already been stated, the author had independently analysed five of these systems, namely, 2, 3, 4, 5 and 7, and had obtained some data for the three sequences which constitute system 6; it is unlikely, however, that he would have succeeded in correlating these sequences without the aid of Dr Mecke's formula for system 6. System 1 was not analysed by the author, as only one sequence had been observed. As a result of the author's observation of a new sequence in system 2 an interpretation different from Dr Mecke's had been arrived at for this system.

While the author's low dispersion data are, of course, far less precise than Frl. Auerbach's excellent grating data in the infra-red, they include several hitherto unrecorded sequences in systems 2, 3, 5 and 7, and also some ultra-violet bands, probably involving some of the electronic energy levels associated with the other systems.

§ 2. THE PRESENT OBSERVATIONS: EXPERIMENTAL DETAILS

The LaO spectrum has been observed as completely as possible from λ 8700 to λ 2850. The source employed was the long yellow flame which projects from a carbon arc freely supplied with lanthanum nitrate and carrying a current of from 15 to 25 amp. The LaO bands are developed much more intensely in this flame than in the arc itself, which, of course, develops the line spectrum of the La atom predominantly. Four spectrographs have been used in different parts of the spectrum:

(i) a quartz prism Littrow instrument having a dispersion varying from 71 to 12·5 Å./mm. over the range λ 8670 to λ 4350; this was used in the initial survey of the whole spectrum;

(ii) a glass prism Littrow spectrograph† (Hilger's E 52), with a dispersion of from 48 to 29 Å./mm. over the range for which it was employed in this instance, namely, λ 8670 to λ 7380;

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* For system 2 the coefficient of n''^2 is given as 3·0 in Dr Mecke's letter, but this is probably a misprint for 2·0, which gives better agreement between the observed and calculated wave numbers.

† In Messrs Adam Hilger's laboratory, at the kind invitation of Mr F. Twyman, F.R.S.

(iii) a glass prism Littrow instrument* of still higher dispersion, namely, from 26 to 18 Å./mm. over the range, λ 8100 to λ 7000, for which it was employed;

(iv) a 2·35 m. concave grating spectrograph, giving a dispersion of about 7·3 Å./mm. in the first order, which was used for system 3. For the extreme red and near infra-red bands Kodak kryptocyanine and neo-cyanine plates were used, the iron arc lines being employed as standards of wave-length in these, as in the more refrangible regions.

§ 3. SYSTEM 3: THE GREEN, YELLOW, AND ORANGE BANDS

This system, which it is convenient to describe first, is the most extensive system in the whole spectrum. In the first order of the grating measures have been made of a pair of heads in a large number of bands of six sequences. The bands previously recorded form but small fragments of the − 1, 0 and − 1 sequences, and only in the case of two bands has more than one head been recorded hitherto.

Table 2. System 3; wave-lengths of *R* and *Q* heads

n', n''	λ_{air}	n', n''	λ_{air}	n', n''	λ_{air}	n', n''	λ_{air}	n', n''	λ_{air}	n', n''	λ_{air}
		2, 0	5178·28 80·00	1, 0	5380·37 82·40	0, 0	5599·91 5602·41	0, 1	5866·27 69·37	0, 2	6157·36 61·24
4, 1	5015·39 —	3, 1	5202·73 04·47	2, 1	5405·57 07·59	1, 1	26·00 28·51	1, 2	93·39 96·53	1, 3	85·66 89·57
5, 2	? 39·60 40·92	4, 2	27·31 29·04	3, 2	30·94 32·96	2, 2	52·27 54·66	2, 3	5920·71 23·78	2, 4	6214·07 17·97
6, 3	63·60 64·99	5, 3	52·13 53·78	4, 3	55·50 58·47	3, 3	78·48 80·90	3, 4	48·07 51·16	3, 5	42·62 46·51
7, 4	87·80 89·21	6, 4	77·03 78·78	5, 4	82·16 84·20	4, 4	5705·07* 07·55	4, 5	75·70 78·72	4, 6	71·31 75·17
8, 5	5112·40 †	7, 5	† 5303·81	6, 5	5508·23 10·18	5, 5	31·65 33·96	5, 6	6003·46 06·48	5, 7	6300·08 03·95
9, 6	36·96 38·12	8, 6	27·79 29·17	7, 6	34·13 36·12			6, 7	31·33 34·27	6, 8	29·09 32·93
10, 7	61·56 ? 62·92	9, 7	53·24 54·62	8, 7	60·27 62·21			7, 8	59·31 62·32	7, 9	57·89 62·05
		10, 8	78·81 ? 79·86	9, 8	86·81 ? 88·71			8, 9	87·70 90·56	8, 10	87·49 91·25
								9, 10	6115·93 18·69	9, 11	6417·01 20·67
								10, 11	44·44 47·37	10, 12	46·50 50·05

* Confused by structure of previous band.

† Hidden by a line.

The wave-lengths are shown in Table 2 and the usual n', n'' arrangement of the wave-numbers of the heads is given in Table 3. Though the visual estimates of the intensities of the bands are not tabulated, it may be stated that they conform to a Condon parabola of maxima; a fact which may be inferred generally from the distribution in Table 3.

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* At the Imperial College, South Kensington, by kind permission of Prof. A. Fowler, F.R.S.

Table 3. Wave-numbers and differences in progressions of system 3. (*R* heads, upper figures; *Q* heads, lower figures.)

n'' / n'	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	17852·5 810·6 44·5 811·7	17041·9 805·7 32·8 806·8	16236·2 26·0											
	728·4 729·4	727·8 729·0	727·3 728·4											
1	18580·9 811·2 73·9 812·1	17769·7 806·2 61·8 807·4	16963·5 801·5 54·4 802·6	16162·0 51·8										
	725·2 725·8	724·6 725·6	723·6 725·6	723·2 724·9										
2	19306·1 811·8 299·7 812·3	18494·3 807·2 87·4 807·8	17687·1 801·9 79·6 802·9	16885·2 797·1 76·7 797·7	16088·1 78·0									
		721·0 721·5	720·8 721·4	720·3 721·3	719·4 720·8									
3		19215·3 807·4 08·9 807·9	18407·9 802·4 01·0 803·0	17605·5 798·0 598·0 799·2	16807·5 793·0 798·8 794·3	16014·5 04·5								
		717·8 —	717·1 717·7	716·2 717·0	716·0 717·0	715·3 716·8								
4		19933·1 808·1 — —	19125·0 803·3 18·7 803·7	18321·7 798·2 15·0 799·2	*17523·5 793·7 15·8 794·5	16729·8 788·6 21·3 789·9	15941·2 31·4							
			712·3 713·4	712·9 713·6	712·4 713·3	712·4 713·8	711·2 712·7							
5			?19837·3 802·7 32·1 803·5	19034·6 798·7 28·6 799·5	18235·9 793·7 29·1 794·0	17442·2 789·8 35·1 791·0	16652·4 784·0 44·1 785·4	15868·4 58·7						
				708·7 709·3	708·9 709·4	707·4 708·1		707·1 708·7						
6				19743·3 798·5 37·9 799·4	18944·8 795·2 38·5 795·3	18149·6 43·2		16575·5 779·8 67·4 781·3	15795·7 86·1					
					704·6 705·5	 705·9			703·2 704·7					
7					19649·4 — 41·0 794·9	† 18849·1 790·9	18064·7 58·2		16498·9 774·8 90·8 776·9	15724·1 13·9				
						— —	699·6 701·2			697·9 700·4				
8						19554·9 790·6 †	18764·3 784·5 59·4 785·9	17979·8 73·5		16422·0 770·7 14·3 772·2	15651·3 42·1			
							697·1 697·6	695·3 696·8			694·9 696·7			
9							19461·4 786·3 57·0 786·7	18675·1 780·8 70·3 782·0	17894·3 88·3?		16346·2 766·9 38·8 768·4	15579·3 70·1		
								693·5 693·2	692·0 694·4			691·1 692·2		
10								19368·6 782·3 363·5 780·8	18586·3 82·7?			16270·4 762·4 62·6 763·1	15508·0 499·5	
11														15437·3 28·9

* Confused by structure of previous band.

† Hidden by a line.

From the fact that the separations in the pairs of heads in Table 3 increase in magnitude with decreasing n' and with increasing n'', as well as from the appearance of the heads in the spectrograms, it is concluded that they are the heads of R and Q branches respectively. The data are closely represented by the following formulae:

$$\begin{aligned}\nu_{R\,\text{head}} &= 17894{\cdot}1 + [732{\cdot}6\,(n'+\tfrac{1}{2}) - 1{\cdot}81\,(n'+\tfrac{1}{2})^2] \\ &\quad - [815{\cdot}5\,(n''+\tfrac{1}{2}) - 2{\cdot}43\,(n''+\tfrac{1}{2})^2] - 0{\cdot}50\,(n'+\tfrac{1}{2})\,(n''+\tfrac{1}{2}); \\ \nu_{Q\,\text{head}} &= 17885{\cdot}8 + [733{\cdot}2\,(n'+\tfrac{1}{2}) - 1{\cdot}88\,(n'+\tfrac{1}{2})^2] \\ &\quad - [816{\cdot}1\,(n''+\tfrac{1}{2}) - 2{\cdot}28\,(n''+\tfrac{1}{2})^2] - 0{\cdot}25\,(n'+\tfrac{1}{2})\,(n''+\tfrac{1}{2}).\end{aligned}$$

The small $(n'+\frac{1}{2})\,(n''+\frac{1}{2})$ term is definitely necessary in the case of the R-head data, and appears also to be required, though less definitely, by the Q-head data; in the latter case it is difficult to evaluate the coefficient satisfactorily, but it is probably of the order 0·25 as given. This, if sustained by still higher dispersion measures, would imply that the Q branch is not of the simplest type in which the head is associated with the rotationless state of the molecule.

At the red end of this system the spectrograms show a group of bands degrading in the opposite direction and probably arising from an impurity in the material used. The presence of these bands renders measurement of the heads of the weak sequence + 3 difficult; incomplete data for some bands of this sequence were obtained but are omitted from the tables.

§ 4. SYSTEMS 4, 5, 6 AND 7: THE EXTREME RED AND NEAR INFRA-RED BANDS

As already mentioned, Kayser has recorded two groups of red bands at λ 6995 and λ 7380, and Frl. Auerbach and the author have, independently of one another, discovered and measured two near infra-red groups at λ 7877 and λ 8453. The data for these four groups are collected in Table 4 which also shows the assignment of the bands to Mecke's systems 4, 5, 6 and 7. The writer's data are from plates taken with the two glass Littrow spectrographs. They are more numerous and more precise than those given by Kayser, and also include some bands not recorded by Frl. Auerbach. With the high dispersion used by Frl. Auerbach many strong heads which are apparently single in the author's spectrograms are found to be a close pair with a separation of the same order as that previously measured by Kellner* and by Ôkubo† in the strong blue-violet bands, about 0·5 cm.$^{-1}$.

It will be seen in Table 4 that alternate bands of the λ 6995 group belong to two sequences, namely, the − 1 sequences of systems 4 and 5. A given band of the latter system is more intense than the corresponding band of the former.

The λ 7379 group is made up of four interlacing sequences, the 0 sequences of systems 4 and 5 accounting mainly for alternate bands at the beginning of the group and the − 1 sequences of systems 6 and 7 for those at the end; the middle of the group where bands of all four systems occur in the order 5, 7, 4, 6 is rather complicated.

In the λ 7877 group the most intense bands form the 0 sequence of system 7; these have been measured by both Frl. Auerbach and the author, as also has the

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* *Dissertation* (Bonn, 1904); and Kayser, *Handbuch*, 5, 667 (1910).

† *Loc. cit.*

Table 4. Systems 4, 5, 6 and 7:

Kayser	Author		n', n'' and $\delta\nu$	
λ	λ_{air}	ν_{vac}	Sys. 4 −1 seq.	Sys. 5 −1 seq.
6995	6994·4	14293·2	1, 0	
7012	7010·9	259·6	60·6	1, 0
7024	24·2	232·6	2, 1	60·4
7041	40·7	199·2	61·6	2, 1
7055	54·7	171·0	3, 2	
7069				60·0
7071	70·6	139·2	61·0	3, 2
7086	85·2	110·0	4, 3	60·4
7101	7100·9	078·8	61·2	4, 3
7117	16·1	048·8	5, 4	60·4
7132	31·5	018·4	61·4	5, 4
7148	47·3	13987·4	6, 5	60·3
7161	62·3	958·1	61·0	6, 5
7179	78·6	926·4	7, 6	60·7
7194	93·6	897·4	61·6	7, 6
	7210·5	864·8	8, 7	60·4
	25·0	837·0	62·0	8, 7
	42·9	802·8	9, 8	60·8
	56·9	776·2	61·6	9, 8
	75·4	741·2	10, 9	61·1
	89·2	715·1	61·0	10, 9
	7307·8	680·2	11, 10	60·8
	21·7	654·3	61·6	11, 10
	40·9	618·6	12, 11	61·0
	54·5	593·3	62·4	12, 11
	74·7	556·2	13, 12	

Kayser	Author		n', n'' and $\delta\nu$			
λ	λ_{air}	ν_{vac}	Sys. 4 0 seq.	Sys. 5 0 seq.	Sys. 6 −1 seq.	Sys. 7 −1 seq.
7380	7379·2	13547·9	0,0			
7404	7402·5	505·2	57·5	0, 0		
7414	10·6	490·4	1,1	55·9		
7434	33·3	449·3	56·9	1, 1		
7444	42·1	433·5	2,2	56·1		
7465	64·4	393·2	57·2	2, 2		
7485	73·8	376·3	3,3	55·7		
7497	95·6	337·5	57·3	3, 3		
	7506·0	319·0	4,4	56·4		
	27·4	281·1	57·9	4, 4		
	38·8	261·1	5,5	56·0		
	59·3	225·1	57·3	5, 5		
	62·7	219·2				4,3
	71·5	203·8	6,6	56·3		
	74·4	198·7			5, 4	59·4
	91·6	168·8	57·3	6, 6		
	96·8	159·8			60·9	5,4
	7604·5	146·5	7,7	55·6		
	09·5	137·8			6, 5	59·5
	23·8	113·2		7, 7		
	31·3	100·3			60·3	6,5
				57·2		
	44·6	077·5			7, 6	59·3
	57·2	056·0		8, 8		
	*66·0	041·0			60·6	7,6
				56·0		
	80·2	016·9			8, 7	59·9
	90·5	000·0		9, 9		
	7701·4	12981·1			59·2	8,7
				55·9		
	15·3	957·7			9, 8	60·3
	23·4	944·1		10, 10		
	37·3	920·8			59·5	9, 8
	50·9	898·2			10, 9	60·6
	73·8	860·2				
	73·8	860·2			62·3	10, 9
	88·5	835·9			11, 10	

* Confused by K line λ 7664·94 which is strongly developed; λ and ν estimated.

0, 0 band of system 6, which is the first band of this group. There are intervening band-heads, not recorded by Frl. Auerbach, which fall into two sequences. One of these, the + 1 sequence of system 5, consists of quite well defined heads, while the other consists of doubtful heads which were measured with some difficulty but were retained on account of their obviously regular spacing. The latter sequence afterwards proved to be the 0 sequence of system 6, but it was only with the aid of Mecke's formula (see Table 1) for this system that the author connected these heads with the well-developed 0, 0 band λ 7877 at the beginning of the group and with the well-defined − 1 sequence in the latter part of the previous (λ 7379) group.

red and infra-red bands

Frl. Auerbach λ_{air}	Frl. Auerbach ν_{vac}	Author λ_{air}	Author ν_{vac}	n', n'' and $\delta\nu$: Sys. 5 −1 seq.	Sys. 6 0 seq.	Sys. 7 0 seq.
7876·867 77·22	12691·92 691·34	7876·5	12692·5		0, 0	
7910·196 10·34	638·45 638·21	7909·5	639·6			0, 0
						54·6
7944·61 44·95	583·69 583·14	7943·8	585·0			1, 1
		7973·6	? 538·0	3, 4		54·9
7979·35 79·70	528·91 528·36	7978·6	530·1			2, 2
				49·7		
		7981·2	? 526·2		3, 3	
						54·9
		8005·3	488·3	4, 5		
					58·0	
8014·430 14·79	474·07 473·51	8013·6	475·2			3, 3
				51·6		
		8018·2	468·2		4, 4	
						54·7
		8038·5	436·7	5, 6		
					55·3	
8049·920 50·26	419·07 418·54	8048·8	420·5			4, 4
				51·9		
		8053·9	412·9		5, 5	
						54·9
		8072·2	384·8	6, 7		
					55·7	
8085·75 86·092	364·01 363·52	8084·7	365·6			5, 5
				51·8		
		8090·2	357·2		6, 6	
						55·4
		8106·1	333·0	7, 8		
					56·4	
8121·87 22·240	309·06 308·49	8121·1	310·2			6, 6
				52·3		
		8127·3	300·8		7, 7	
						54·8
		8140·6	280·7	8, 9		
					55·7	
8158·76 59·105	253·40 252·88	8157·4	255·4			7, 7
				53·1		
		8164·3	245·1		8, 8	
						55·2
		8176·0	227·6	9, 10		
					56·4	
8195·60 96·00	198·32 197·72	8194·3	200·2			8, 8
				52·2		
		8202·1	188·7		9, 9	
						57·2
		8211·0	175·4	10, 11		
8232·94	143·00					9, 9

Frl. Auerbach λ_{air}	Frl. Auerbach ν_{vac}	Author λ_{air}	Author ν_{vac}	n', n'' and $\delta\nu$: Sys. 6 +1 seq.	Sys. 7 +1 seq.
		8408	11890	0, 1	
				48·4	
		8442·5	841·6	1, 2	
8453·412 53·742	11826·30 825·83	8452·8	827·1		0, 1
					51·4
8489·627 89·996	775·85 775·34	8489·7	775·7		1, 2
					50·2
8526·216 26·622	725·32 724·76	8526·1	725·5		2, 3
		8542·8	702·6		51·0
8564·025 64·366	673·55 673·09	8563·1	674·5		3, 4
					50·6
8600·463 00·810	624·09 623·62	8600·6	623·9		4, 5
					49·2
8638·129 38·460	573·40 572·96	8637·1	574·7		5, 6
		8644·3	565·1		
		8666·4	? 535·7		

The λ 8453 group consists chiefly of a sequence of bands which have been measured by both Frl. Auerbach and the author, namely, the + 1 sequence of the relatively intense system 7. The author's plates show in addition a few fainter heads, two of which fall into the + 1 sequence of the weaker system 6.

The usual n', n'' arrangement of the wave numbers of the heads is shown in Table 5 for systems 4 and 5, in Table 6 for systems 6 and 7; the reason for pairing neighbouring systems in this way will be apparent presently. In each of these four systems a strong 0 sequence is observed with either one or both of the neighbouring sequences − 1 and + 1; this distribution of intensity is characteristic of a relatively

Table 5. Wave-numbers and differences in progressions of systems 5 (upper figures) and 4 (lower figures)

n″ n′	0		1		2		3		4		5		6		7		8		9		10		11	12
0	13505·2 13547·9		*																					
	754·4 745·3																							
1	14259·6 14293·2	810·3 802·8	13449·3 13490·4		†																			
			749·9 742·2																					
2			14199·2 14232·6	806·0 799·1	13393·2 13433·5		‡																	
					746·0 737·5																			
3					14139·2 14171·0	801·7 794·7	13337·5 13376·3	799·5 —	12538·0? —															
							741·3 733·7		743·1 —															
4							14078·8 14110·0	797·7 791·0	13281·1 13319·0	792·8 —	12488·3 —													
									737·3 729·8		736·8 —													
5									14018·4 14048·8	793·3 787·7	13225·1 13261·1	788·4 —	12436·7 —											
											733·0 726·3		732·1 —											
6											13958·1 13987·4	789·3 783·6	13168·8 13203·8	784·0 —	12384·8 —									
													728·6 722·6		728·4									
7													13897·4 13926·4	784·2 779·9	13113·2 13146·5	780·2 —	12333·0 —							
															723·8 718·3		723·0 —							
8															13837·0 13864·8	781·0 —	13056·0 —	775·3 —	12280·7 —					
																	720·2		719·3					
9																	13776·2 13802·8	776·2 —	13000·0 —	772·4 —	12227·6			
																			715·1		716·5 —			
10																			13715·1 13741·2	771·0 —	12944·1 —	768·7 —	12175·4 —	
																					710·2			
11																					13654·3 13680·2			
12																							13593·3 13618·2	
13																								— 13556·2

* Hidden by 0, 0 band of system 6. † Hidden by 0, 0 band of system 7. ‡ Hidden by 1, 1 band of system 7.

Table 6. Wave-numbers and differences in progressions of systems 7 (upper figures) and 6 (lower figures)

n′ \ n″	0		1		2		3		4		5		6		7		8		9
0	12639·6 12692·5	812·5 802·5	11827·1 11890																
			757·9 —																
1			12585·0 *	809·3 —	11775·7 11841·6														
					754·4 —														
2					12530·1 †	804·6 —	11725·5 —												
							749·7 —												
3							12475·2 ?12526·2	800·7 —	11674·5 —										
							744·0 —		746·0 —										
4							13219·2 —	798·7 —	12420·5 12468·2	796·6 —	11623·9 —								
									739·3 730·5		741·7 —								
5									13159·8 13198·7	794·2 785·8	12365·6 12412·9	790·9 —	11574·7 —						
											734·7 724·9		735·5 —						
6											13100·3 13137·8	790·1 780·6	12310·2 12357·2						
													730·8 720·3						
7													‡13041 13077·5	785·7 776·7	12255·4 12300·8				
															725·7 716·1				
8															12981·1 13016·9	780·9 771·8	12200·2 12245·1		
																	720·6 712·6		
9																	12920·8 12957·7	— 769·0	— 12188·7
																			— 709·5
10																			12860·2 12898·2

* Hidden by 0, 0 band of system 7. † Hidden by 1, 1 band of system 7. ‡ Confused by K line λ 7664·94; ν estimated.

small change of vibration frequency and of moment of inertia in passing from the initial to the final state of the molecule—a smaller change than that represented by the more open "parabolic" distribution of system 3 (Table 3). This is also seen in the formulae which have been derived from the data, namely:

System

4. $\nu = 13576{\cdot}5 + [749{\cdot}3\,(n' + \tfrac{1}{2}) - 1{\cdot}93\,(n' + \tfrac{1}{2})^2] - [806{\cdot}4\,(n'' + \tfrac{1}{2}) - 1{\cdot}89\,(n'' + \tfrac{1}{2})^2]$.

5. $\nu = 13532{\cdot}4 + [759{\cdot}1\,(n' + \tfrac{1}{2}) - 2{\cdot}21\,(n' + \tfrac{1}{2})^2] - [814{\cdot}9\,(n'' + \tfrac{1}{2}) - 2{\cdot}20\,(n'' + \tfrac{1}{2})^2]$.

6. $\nu = 12721{\cdot}1 + [750{\cdot}2\,(n' + \tfrac{1}{2}) - 2{\cdot}08\,(n' + \tfrac{1}{2})^2] - [806{\cdot}6\,(n'' + \tfrac{1}{2}) - 2{\cdot}13\,(n'' + \tfrac{1}{2})^2]$.

7. $\nu = 12668{\cdot}1 + [762{\cdot}8\,(n' + \tfrac{1}{2}) - 2{\cdot}29\,(n' - \tfrac{1}{2})^2] - [818{\cdot}5\,(n'' - \tfrac{1}{2}) - 2{\cdot}37\,(n'' - \tfrac{1}{2})^2]$.

It is clear from the coefficients that systems 5 and 7 resemble one another, as also do systems 4 and 6. If due allowance be made for the small dispersion used in the infra-red, it will be seen on comparison of the [″] terms in these formulae with those in the formulae already given for system 3, that systems 3, 5 and 7 probably have the same final state; Mecke has independently reached the same conclusion (*a*), p. 521. This is more definitely indicated by a direct comparison of the vibration frequency differences for these three systems in Tables 3, 5 and 6 than by the coefficients in the formulae.

Systems 4 and 6 are somewhat alike both in their appearance in the spectrograms and in the values of the vibrational frequency differences associated with their initial and final states. Comparison, either by means of the above formulae or by means of the differences in the progressions in Tables 5 and 6, is less conclusive than in the case of systems 5 and 7 on account of the inadequacy of the data for system 6, but it is improbable that 4 and 6 have either a common initial or a common final state.

It is interesting to study these systems from another point of view. In Table 5 it will be seen that the interval between the heads of corresponding bands of systems 4 and 5 increases with decreasing n' in the n' progressions and with increasing n'' in the n'' progressions; and Table 6 shows a similar variation of the interval between the heads of corresponding bands of systems 6 and 7. This is exactly the kind of variation which is shown by the interval $\nu_{R\,\text{head}} - \nu_{Q\,\text{head}}$ in a system of single bands of the *PQR* type, such as system 3 described in the previous section. Hence these observations are in harmony with the interpretation of systems 4 and 5 as a single system, in which 4 represents the *R* heads and 5 the *Q* heads, and of systems 6 and 7 as a similar system of bands with *R* and *Q* heads. According to this view, 4, 5 and 6, 7 are a pair of systems forming an electronic doublet with a common final electronic energy level and a pair of initial electronic energy levels having a separation $\Delta\nu = \nu_5 - \nu_7 = 13532{\cdot}4 - 12668{\cdot}1 = 846{\cdot}1$ cm.$^{-1}$. For so heavy a molecule as LaO this wide doublet separation is perhaps quite reasonable.

Further, it seems likely that the electronic energy level of the LaO molecule, with 65 extra-nuclear electrons, may be comparable with those of the Cs atom which contains ten fewer electrons[*] and that the pair of systems 7, 6 and 5, 4 may be the LaO counterpart of the Cs doublet $\lambda\lambda$ 8942·46, 8521·12 which is given by transitions from the lowest pair of excited states $6\,^2P_{\frac{1}{2}}$, $6\,^2P_{1\frac{1}{2}}$, to the normal state $6\,^2S_{\frac{1}{2}}$ of the Cs atom. This would imply that the band-systems are due to transitions $^2\Pi \rightarrow {}^2\Sigma$, the common final $^2\Sigma$ state being the normal state of the molecule, and the initial $^2\Pi$ states the lowest two excited states; the doublet separation in Cs, $^2P_{1\frac{1}{2}} - {}^2P_{\frac{1}{2}} = 11732{\cdot}3 - 11178{\cdot}3 = 554$ cm.$^{-1}$, and in LaO $^2\Pi_{1\frac{1}{2}} - {}^2\Pi_{\frac{1}{2}} = 864$ cm.$^{-1}$, which is not unreasonable.

We must now see whether the intervals 4–5 and 6–7, which are about 44 and 53 cm.$^{-1}$ respectively, are of the order of magnitude to be expected for $\nu_{R\,\text{head}} - \nu_{Q\,\text{head}}$ when compared with system 3 in which this interval is about 8 cm.$^{-1}$ Now the interval $\nu_{R\,\text{head}} - \nu_{Q\,\text{head}} = h/8\pi^2c(I_0' - I_0'')$ in the 0, 0 band; i.e. it is inversely proportional to the change in the moment of inertia of the molecule in the initial and final states. But $(I_0' - I_0'')$ increases and decreases in magnitude with $(\omega_0'' - \omega_0')$, the change in the vibrational frequency, which in systems 4, 5, 6 and 7 is only about two-thirds of the value in system 3, as may be seen from the foregoing formulae. Hence we should expect $\nu_{R\,\text{head}} - \nu_{Q\,\text{head}}$ to be larger in the systems 4, 5 and 6, 7 than in system 3, though not perhaps so much as 44/8 or 53/8 times. Here, then, appears to be evidence against the coupling of the systems, the intervals 4–5 and 6–7 being apparently too large.

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[*] Mr R. W. B. Pearse has suggested to the author that the basis of this comparison may be that in oxides, fluorides, etc. (but not hydrides) of heavy metallic atoms each constituent atom of the molecule not only retains its own two K electrons, but also has a complete group of eight L electrons independently of the presence of the other constituent atom, and that the remaining electrons constitute an outer structure of the whole molecule similar to that of the atom with ten fewer electrons. Thus we have the following comparable atomic and molecular electron configurations:

Atoms		K	L	M	N	O	P	Molecules		K, K	L, L	Outer			
K, Ca^+	(19)	2	8	8	1	–	–	ScO, CaF	(29)	2, 2	8, 8	8	1	–	–
Rb, Sr^+	(37)	2	8	18	8	1	–	YO, SrF	(47)	2, 2	8, 8	18	8	1	–
Cs, Ba^+	(55)	2	8	18	18	8	1	LaO, BaF	(65)	2, 2	8, 8	18	18	8	1
Ca	(20)	2	8	8	2	–	–	TiO	(30)	2, 2	8, 8	8	2	–	–
Sr	(38)	2	8	18	8	2	–	ZrO	(48)	2, 2	8, 8	18	8	2	–
Ba	(56)	2	8	18	18	8	2	HfO	(66)	2, 2	8, 8	18	18	8	2

From this point of view Miss F. Lowater, *Nature*, **123**, 644 (1929), has recently examined the band systems of TiO, and the writer is investigating those of ScO and YO. R. C. Johnson's comparison of the energy levels of CaF, SrF and BaF with those of Ca^+, Sr^+ and Ba^+ (*Proc. Roy. Soc.* A, **122**, 161, 189 (1929)) is of a similar nature, though the electron structures suggested by Johnson differ from those adumbrated by Pearse. In 1925 Mulliken, *Phys. Rev.* **26**, 562 (1925), compared some light diatomic molecules with the atom containing ten less electrons; e.g. BeF, BO, CN, CO^+, N_2^+ (13 electrons) with Li, and MgF, AlO, SiN (21 electrons) with Na, but they have usually been compared, by Mulliken and others, with the atom having two fewer electrons, the constituent atoms of the molecule being supposed to retain only their K electrons; thus:

Atoms		K	L	M	N	Molecules		K, K	Outer		
Na	(11)	2	8	1	–	BO, BeF	(13)	2, 2	8	1	–
K	(19)	2	8	8	1	AlO, MgF	(21)	2, 2	8	8	1
Mg	(12)	2	8	2	–	CO, N_2	(14)	2, 2	8	2	–
Ca	(20)	2	8	8	2	SiO, CS	(22)	2, 2	8	8	2

§ 5. SYSTEMS 1 AND 2; THE BLUE-VIOLET BANDS

The bands in the blue-violet region occur in five short ranges and are accordingly shown in five divisions of Table 7:

(*a*) An apparently continuous range, beginning with a fairly well defined edge at λ 4348·2 and extending with gradually increasing intensity to λ 4371·9. The quartz Littrow spectrograph reveals no definite division into a sequence of bands but there appear to be two vague heads at about 21 and 43 cm.$^{-1}$ respectively from the edge.

(*b*) The sequence of very strong bands beginning at λ 4371·9 and occurring at intervals of about 20 cm.$^{-1}$. The heads of these bands have been measured under high dispersion by Kellner and by Ôkubo and found to be very close doublets with a separation of about 0·5 cm.$^{-1}$, which has also been found in system 7 by Frl. Auerbach. This is the 0 sequence of Mecke's system 1.

(*c*) A similar and equally strong sequence of bands beginning at λ 4418·2 and occurring at rather greater intervals, about 25 cm.$^{-1}$; the doublet separation as measured by both Kellner and Ôkubo is again about 0·5 cm.$^{-1}$ This is the 0 sequence of Mecke's system 2.

(*d*) Some faint bands running on from the end of (*c*) to about λ 4500, and followed by a range of apparently continuous spectrum between about λ 4535 and about λ 4560, in which no band-heads can be measured on the quartz spectrograms.

(*e*) A sequence of regularly spaced bands similar to, but very much weaker than, (*b*) and (*c*), beginning at λ 4580·8 and occurring at intervals of about 20 cm.$^{-1}$. They have been measured on plates taken with the quartz spectrograph (dispersion here about 15 Å./mm.). Though the heads appear to be single, it is probable that under adequate dispersion they would be found to be double, like (*b*) and (*c*), with a separation of about 0·5 cm.$^{-1}$.

Spectrograms in which (*a*), (*d*) and (*e*) are measurable show (*b*) and (*c*) very much over-exposed. For the two latter Ôkubo's [I.A.] data, which are more complete than Kellner's [R.A.] data, are included in Table 7 with the writer's observations of (*a*), (*d*) and (*e*).

System 2. According to Mecke's formula for system 2, the coefficients of which have been given in Table 1, the 0 sequence is (*c*) as would be expected, and the + 1 sequence is (*e*) with the first band λ 4580·8 omitted. There is, in fact, no place in Mecke's system 2 for this band, although in the writer's plates it clearly belongs to the same sequence as the rest in (*e*) and is just as genuine a band as the next band λ 4585·0 which is the 0, 1 band in Mecke's system. According to the writer's assignment of n', n'' values, which is shown in Tables 7 and 8, λ 4580·8 is the 0, 1 band, and the system is approximately represented by the formula

$$\nu = 22639{\cdot}5 + [782{\cdot}7\,(n' + \tfrac{1}{2}) - 2{\cdot}39\,(n' + \tfrac{1}{2})^2] - [807{\cdot}3\,(n'' + \tfrac{1}{2}) - 2{\cdot}27\,(n'' + \tfrac{1}{2})^2].$$

This expression shows at once that the change in vibration frequency $(\omega'' - \omega')$, and therefore in moment of inertia $(I' - I'')$ for this system, is even smaller than the changes in systems 4, 5, 6 and 7; the intensity distribution is in full accordance

Table 7. Systems 1 and 2 and other blue-violet bands

(a)

λ_{air} (Author)	$\nu_{vac.}$ and $\delta\nu$
4348·2	22991·6
	21·1
52·2	970·5
	21·7
56·3	948·8

These are faint heads (?) in apparently continuous spectrum from the edge at λ 4348·2 to the very strong head λ 4371·9 (0, 0 of system 1)

(b)

λ air (Ôkubo)	$\nu_{vac.}$ and $\delta\nu$	n', n'' Sys. 1
4371·869 ·974	22867·11 66·56	0,0
	20·14 20·12	
75·722 ·821	46·97 46·44	1,1
	20·54 20·54	
79·660 ·762	26·43 25·90	2,2
	20·08 19·81	
83·517 ·567	06·35 06·09	3,3
	20·61 20·98	
87·482 ·603	22785·74 85·11	4,4
	21·60 21·47	
91·644 ·741	64·14 63·64	5,5
	20·77 20·72	
95·655 ·742	43·37 42·92	6,6
	22·69 22·65	
4400·045 ·125	20·68 20·27	7,7
	24·22 24·29	
04·741 ·833	22696·46 95·98	8,8

(c)

λ air (Ôkubo)	$\nu_{vac.}$ and $\delta\nu$	n', n'' Sys. 2
4418·170 ·265	22627·47 26·99	0,0
	25·25 25·19	
23·106 ·188	02·22 01·80	1,1
	25·16 25·25	
28·036 ·136	22577·06 76·55	2,2
	25·33 25·08	
33·008 ·060	51·73 51·47	3,3
	25·07 25·40	
37·942 38·060	26·66 26·07	4,4
	25·99 25·89	
43·070 ·165	00·67 00·18	5,5
	25·90 25·93	
48·190 ·293	22474·77 74·25	6,6
	26·25 26·19	
53·391 ·481	48·52 48·06	7,7
	26·65 —	
58·684 —	21·87 —	8,8
	? 28·55 —	
? 64·368 —	22393·32 —	9,9

For 9, 9 the writer's measure is

λ air	$\nu_{vac.}$ and $\delta\nu$
	26·6
4463·98	22395·3

(d)

λ_{air} (Author)	$\nu_{vac.}$
4468·7?	22371·6
71·1	359·6
73·0?	350·1
79·6	317·2
81·0?	310·2
83·6?	297·3
85·8	286·3
89·1	270·0
91·4	258·5

and unresolved spectrum from about λ 4535 to about λ 4560

(e)

λ_{air} (Author)	$\nu_{vac.}$ and $\delta\nu$	n', n'' Sys. 2
4580·78	21824·2	0, 1
	20·0	
85·00	804·2	1, 2
	20·9	
89·39	783·3	2, 3
	20·3	
93·68	763·0	3, 4
	21·1	
98·14	741·9	4, 5
	20·7	
4602·51	721·2	5, 6
	22·4	
07·26	698·8	6, 7
	21·4	
11·82	677·4	7, 8
	23·7	
16·85	653·7	8, 9
	26·8	
22·58	626·9	9, 10

Table 8. Wave-numbers and differences in progressions of system 2

n' \ n''	0	1	2	3	4	5	6	7	8	9	10
0	22627·5 803·3	21824·2									
		778·0									
1		22602·2 798·0	21804·2								
			772·8								
2			22577·0 793·7	21783·3							
				768·4							
3				22551·7 788·7	21763·0						
					763·6						
4					22526·6 784·7	21741·9					
						758·8					
5						22500·7 779·5	21721·2				
							753·6				
6							22474·8 776·0	21698·8			
								749·7			
7								22448·5 771·1	21677·4		
									744·5		
8									22421·9 768·2	21653·7	
										739·6	
9										22393·3 766·4	21626·9

with so small a change, the 0 sequence being very much more intense than the + 1 sequence, and the − 1 sequence being not even detected (the 1, 0 band should be at λ 4271·4).

From Mecke's analysis it appears that the initial state for system 2 is the same as the final state for system 6: see conclusion (*d*) on p. 522. The interpretation here suggested, however, conflicts with this conclusion, and appears to show rather that if systems 2 and 6 have a state in common it is the final state of both. This may be seen either by comparing the [″] term in the above formula and the system 6 formula given on p. 530, or by comparing the vibration frequency differences in the n'' progressions of the systems in Tables 6 and 8, due allowance being made for the fact that the observations of system 6 are less satisfactory than those of the other systems.

System 1. Mecke's expression for this system (see p. 522) is based on the interpretation of (*b*) of Table 7 as the 0 sequence, and indicates that the + 1 sequence should begin at λ 4535·5 (0, 1), where the writer's plates show the unresolved range (*d*), and that the − 1 sequence should begin at λ 4224, where no bands can be detected in these plates. If we accept Mecke's analysis for system 1 and the present interpretation of system 2, the common state for these two systems can only be the initial of system 1 and the final of system 2, rather than the final of each as concluded by Mecke, see (*b*), p. 522. This, however, seems less probable than either of the following alternatives.

First, we may assume as correct Mecke's conclusion that systems 1 and 2 have a common final state, but suppose it to have vibrational energy levels given by the [″] term now found for system 2 instead of the term given by Mecke, namely $826{\cdot}5\,(n''+\frac{1}{2}) - 2{\cdot}0\,(n''+\frac{1}{2})^2$. We then derive for the observed sequence of system 1 the formula

$$\nu = 22876{\cdot}8 + [788{\cdot}2\,(n'+\tfrac{1}{2}) - 2{\cdot}52\,(n'+\tfrac{1}{2})^2] - [807{\cdot}3\,(n''+\tfrac{1}{2}) - 2{\cdot}27\,(n''+\tfrac{1}{2})^2],$$

which shows that the initial state is different for any state involved in the other systems, and so conflicts with Mecke's suggestion (*c*), p. 522, that the initial state of system 1 is the final state of system 4.

Alternatively we may assume, until prohibited by the discovery of an additional sequence of system 1, that systems 1 and 2 have a common initial state, with vibrational energy levels given by the [′] term now found for system 2. The observed sequence of system 1 is then represented by

$$\nu = 22876{\cdot}8 + [782{\cdot}7\,(n'+\tfrac{1}{2}) - 2{\cdot}39\,(n'+\tfrac{1}{2})^2] - [801{\cdot}8\,(n''+\tfrac{1}{2}) - 2{\cdot}14\,(n''+\tfrac{1}{2})^2],$$

which shows that the final state is not one of those involved in any other system.

These systems have several unusual features: e.g. a gradual increase, instead of decrease, of the interval between consecutive bands in each sequence with increasing n', n''. It may be noted also that, according to Ôkubo's measurements, the 3, 3 band of each system has an interval between its heads about half as large as that in most of the bands; for each of these two bands Kellner measured only the second head.

§ 6. ULTRA-VIOLET BANDS

Band structure extends, with very little interruption, from about λ 3800 to λ 3450 with great complexity in several parts of the range. All the bands whose heads are measurable degrade towards the further ultra-violet, i.e. in the opposite direction to those of the systems already described. They form fragments of several sequences, which clearly belong to more than one band-system. Details of observations made with the quartz Littrow spectrograph are shown in Table 9; in this region the dispersion of the instrument becomes usefully large, being on an average about equal to that of the first order of the 2·35 m. grating.

Table 9. Heads of ultra-violet bands (degraded towards the further ultra-violet)

Intensity	λ_{air}	$\nu_{\text{vac.}}$ and $\delta\nu$	Notes
3	3709·64	26949·2	*†
1	3672·32	27223·0	
		43·7	
2	66·44	267·7	
		39·9	
2	60·94	307·6	
		36·3	
2?	56·08	343·9	*
			‡
6	14·86	655·7	
6?	14·49	658·6	§
		25·8	
6	11·50	681·5	
		26·1	
6	08·09	707·6	
		27·1	
6	04·57	734·7	‖
5	3566·18	28033·2	
5?	65·91	035·4	
		39·0	
4	60·95	074·4	
		36·3	
3	56·35	110·7	
		34·0	
2	52·05	144·7	
1	09·57	485·4	
2?	09·28	487·8	§
1	05·60	517·7	
1	3457·11	917·7	

* Head confused with a line.

† This is the strongest of several bands, the heads of which cannot be located definitely.

‡ Heavier band structure occurs in the ranges λ 3650–λ 3630 and λ 3625–λ 3616, but no heads are measurable.

§ Possibly a line.

‖ The band structure from these four strong heads extends to about λ 3575. There is not a trace of the CN heads, λλ 3590·4, 3585·9, 3583·9.

Though no complete system can be traced, it may be noted briefly that eight of the observed bands appear to belong to two sequences of one system, as shown in Table 10.

Table 10. Part of ultra-violet system

n' ↓		→		n''		
27223·0						
810·2						
28033·2	765·5	27257·7				
		806·7				
		28074·4	766·8	27307·6		
				803·1		
				28110·7	766·8	27343·9
						800·8
						28144·7

The probable significance of this lies in the fact that it exhibits vibrational frequency differences of the same orders of magnitude as those in some of the systems already described, but with the larger differences now in the n' progressions instead of the n'' progressions as in the former systems; this, of course, should be the case in a system of bands degraded towards the ultra-violet. The system suggested by these bands would appear to have as initial state the final state of one or more of the other systems, e.g. 3, 5 and 7, and as final state the initial state of system 1 or 2. Exactly which systems are involved in this combination is uncertain because n', n'' assignments are not possible at present. If systems 5 and 7 are, in fact, involved they cannot represent the electronic doublet corresponding to the infra-red $^2P \rightarrow {}^2S$ doublet of Cs as discussed on p. 531, their final state being an excited, and not the normal, state.

§ 7. SUMMARY OF CONCLUSIONS

The results of the analysis described in the foregoing sections are collected in Table 11, which shows the coefficients in the formulae which have been obtained from the present observations for the band-heads of the seven systems. By means of this and Table 1 we may readily compare the present results with Mecke's. The initial vibration frequencies, and also the final vibration frequencies, are of so nearly the same order of magnitude that the identification of a given electronic state in different systems is at present a matter of some uncertainty; for this purpose it is better to compare the observed frequency differences in the progressions of the systems than to compare the coefficients in their formulae. The following deductions are made:

Table 11. System origins and vibrational frequency coefficients. (Author)

System	$(\nu_e + \kappa)$	Initial state		Final state	
		a'	b'	a''	b''
1	22876·8	Either 788·2	2·52	807·3	2·27
		Or 782·7	2·39	801·8	2·14
2	22639·5	782·7	2·39	807·3	2·27
3 R	17894·1	732·6	1·81	815·5	2·43
3 Q	17885·8	733·2	1·88	816·1	2·28*
4	13576·5	749·3	1·93	806·4	1·89
5	13532·4	759·1	2·21	814·9	2·20
6	12721·1	750·2	2·08	806·6	2·13
7	12688·1	762·8	2·29	818·5	2·37

* These coefficients for system 3 apply only if the small terms in $(n' + \frac{1}{2})(n'' + \frac{1}{2})$, given on p. 525, but omitted here, are included.

(i) Mecke's conclusion (*a*), p. 521, that systems 3, 5 and 7 have a common final state is approximately confirmed by the present observations. (It may be noted that Mecke's formulae for systems 5 and 7 are apparently derived with the same [″] term for each, while the author's are obtained quite independently of one another from the data for the individual systems.)

(ii) The chief differences between the results arise from the fact that system 2 is differently interpreted. The author's interpretation of system 2 does not necessarily imply that Mecke's conclusion (*b*), p. 522, that systems 1 and 2 have a common final state, needs revision. These two systems have one state in common, but with the data yet available it may be either the initial or the final state of each.

(iii) Mecke's suggestion (*c*), p. 522, that the initial state for system 1 may be the final for system 4 is no longer tenable if (ii) is accepted; if these two systems have a state in common it can only be the final of each.

(iv) Similarly, while Mecke suggests, (*d*), p. 522, that the initial state for system 2 may be the final for system 6, the present analysis shows that these two systems probably have a common final state.

(v) Systems 4 and 6 are very much alike, but from the data at present available for the latter it is improbable that they have a common initial or a common final state. It may be that 4 and 5 form one system of *R* and *Q* heads and that 6 and 7 form another similar system, the pair having a common final state and initial states differing by 864 cm.$^{-1}$, and possibly corresponding to the Cs strong infra-red doublet $^2P \rightarrow {}^2S$ in which Δ^2P is 554 cm.$^{-1}$ There are, however, arguments against this view.

(vi) Some ultra-violet bands degraded in the opposite direction to those of systems 1–7 have been observed; although no complete system can be traced it is probable that some of the bands belong to an eighth system which is due to transition from the final state of one or more of the above systems, e.g. 3, 5, 7, to the initial state of another, e.g. 1 or 2.

§ 8. ACKNOWLEDGMENTS

The author has much pleasure in expressing his thanks to Prof. A. Fowler, F.R.S., for the use of a large Littrow glass prism spectrograph at the Imperial College, to Messrs Adam Hilger, Ltd., for the use of an E 52 spectrograph, and to the Government Grant Committee of the Royal Society for a Hilger plate-measuring micrometer and for the prism and lens of the quartz Littrow spectrograph.

APPENDIX

A NOTE ON THE ELECTRONIC BAND SPECTRA OF DIATOMIC MOLECULES

As no account of the analysis of a band spectrum has hitherto been read before the Physical Society, the writer has been asked to add, as an appendix, an explanatory general note.

Theory and experiment agree in attributing line spectra to atoms and band spectra to molecules. The spectra of diatomic molecules, with which we are at present concerned, are of the type which used to be aptly described as "fluted spectra." Examined under low dispersion, each *band* or "fluting" has a sharp edge or *head* from which the intensity falls off in the direction of either increasing wave-number* (in which case the band is said to *degrade* towards the ultra-violet) or decreasing wave-number (band degraded towards the infra-red). In many spectra it is easy to recognise a *sequence* of neighbouring bands distributed with obvious regularity over a limited range; and a number of such sequences constitute a band-*system*. The entire *spectrum* of one molecule consists of a number of systems.

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* Number of waves in 1 cm. *in vacuo* = $\nu_{\text{vac}} = 10^8/(\lambda_{\text{vac}}$ in Å.U.) cm.$^{-1}$.

Thus the well-known *band* of CN with a *head* near λ 3883 is the first of a *sequence* in which the succeeding band-heads are near λλ 3871, 3862, 3854. This sequence and three others, whose first (longest-wave) band-heads are near λ 4606, λ 4216 and λ 3590 respectively, constitute the so-called "violet" *system* of CN, in which all* the bands degrade to the ultra-violet. In the CN *spectrum* there is one other known system, the "red" system, in which all the bands degrade towards the infra-red.

With sufficiently high resolving power a single band is seen to consist of a very large number of closely spaced band-*lines*, which were recognised by early investigators as belonging to two or more series in which the spacing is immeasurably small at the head, and increases at first rapidly and afterwards more slowly with increasing distance from the head, the intensities of the lines at the same time diminishing. The strongest lines are not in general those at the head, the high intensity of the head being due to close packing rather than to high individual intensities of the lines. This early division of a band into series has given place to the present division into *branches*, the word *series* now being reserved for an entirely different purpose, namely, to designate a succession of systems which are found in a few molecular spectra (notably H_2 and He_2) to follow the Rydberg-Ritz distribution which is more often found in atomic line spectra.

In molecular, as in atomic, spectra the theory attributes the emission of a line of wave-number ν cm.$^{-1}$ (frequency νc sec.$^{-1}$) to a transition in the emitter from an excited state (or energy level) in which the energy is E' to a less excited, or the unexcited, state, of energy E'', in accordance with the quantum condition $h\nu c = E' - E''$. The absorption of the same line accompanies the opposite transition $E'' \rightarrow E'$. Whereas the total energy E of an atom in a given state is regarded as almost entirely electronic, E_e, that of a molecule is regarded somewhat arbitrarily as the sum of several parts, the chief of which are electronic energy (E_e), energy of nuclear vibration (E_n), and energy of molecular rotation (E_m), where $E_e > E_n > E_m$. In other words, a molecule has a number of fairly widely spaced *electronic* energy levels (specified by a group of electronic quantum numbers collectively denoted by e); each electronic level has associated with it a set of more closely spaced *vibrational* energy levels (specified by successive values of a vibrational quantum number n), and each of these has a set of much more closely spaced *rotational* energy levels (specified by successive values of a rotational quantum number j, of which m is the component† measuring the nuclear angular momentum in units $h/2\pi$). Thus the wave-number of the line emitted in a transition $E' \rightarrow E''$, the $'$ and $''$ denoting the more excited and the less excited states respectively, is

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* Excepting, for sake of strict accuracy, certain bands known as the "tail bands."

† The other components of j, which measure the electronic angular momentum in units $h/2\pi$, will not be considered in this note. Formerly m was regarded as the true quantum number, but now it is the *total* and not the *nuclear* angular momentum that is quantised, and j takes integral or half-integral values increasing by unity, while generally m does not.

$$\begin{aligned} \nu &= \{(E_e' + E_n' + E_m') - (E_e'' + E_n'' + E_m'')\}/hc \\ &= (E_e' - E_e'')/hc + (E_n' - E_n'')/hc + (E_m' - E_m'')/hc \\ &= \nu_e + \nu_n + \nu_m \qquad \text{......(1)}, \end{aligned}$$

where ν_e, ν_n and ν_m are regarded as three parts of the whole ν, and $\nu_e > \nu_n > \nu_m$ in the general case when E_e, E_n and E_m all change. For a given band ν_m varies from line to line, while $\nu_e + \nu_n$ is constant and defines the *band-origin* ($\nu_m = 0$). For a given system ν_n varies from band to band, ν_e being constant and defining the *system-origin* ($\nu_n = 0$, $\nu_m = 0$).

A system for which both $\nu_e = 0$ and $\nu_n = 0$ consists of a single band known as a *rotation* band; ν_m is so small that such bands are found only in the far infra-red. A system for which $\nu_e = 0$ but $\nu_n \neq 0$ is known as a *vibration-rotation* band-system; ν_n is so much greater than ν_m that such bands lie in the nearer infra-red. A system for which $\nu_e \neq 0$ is known as an *electronic* band-system; ν_e is such that these systems occur anywhere from the near infra-red to the Lyman region. In this note we must briefly consider only the third type.

The energy of an harmonic vibration of the molecule is given by

$$E_n = hc\,\omega_0\,\{(n + \tfrac{1}{2}) - x\,(n + \tfrac{1}{2})^2\}, \quad n = 0, 1, 2, 3, \ldots \qquad \text{......(2)},$$

according to the new quantum mechanics*, $c\omega_0$ sec.$^{-1}$ (or ω_0 cm.$^{-1}$) being the frequency of vibration of infinitesimal amplitude for the non-rotating molecule, and x a small constant ($x = 0$ for simple harmonic vibration). The electronic transition involves changes in both ω_0 and x, and for the band-*origins* in the system arising from the transition we have*

$$\begin{aligned} \nu_0 &= \nu_e + (E_n' - E_n'')/hc \qquad \text{......(3)}. \\ &= \nu_e + [\omega_0'(n' + \tfrac{1}{2}) - \omega_0'x'(n' + \tfrac{1}{2})^2] - [\omega_0''(n'' + \tfrac{1}{2}) - \omega_0''x''(n'' + \tfrac{1}{2})^2] \end{aligned}$$

Since ν_e (or $E_e' - E_e''$) is positive and large compared with ν_n (or $E_n' - E_n''$), the latter may be positive, zero, or negative, and the values of $n'' - n'$ for the bands may accordingly be of either sign (not restricted to ± 1) or zero.

As the positions of the *origins* are known for comparatively few bands, we must consider the positions of the band-heads, by discussing briefly the line structure of a simple type of electronic band. The energy of rotation of a molecule may be written as $E_m = hc.F(j)$, where $F(j)$ is a function which differs in form from one electronic state of the molecule to another. Its simplest forms are $Bj(j + 1)$ and $B(j + \tfrac{1}{2})^2$ where $B = h/8\pi^2 cI = 27 \times 10^{-40}/I$, I being the moment of inertia of the molecule. Much more complicated forms of $F(j)$ are frequently necessary.

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* The older quantum theory gave:

$$E_n = hc\omega_0\,(n - xn^2), \quad n = 0, 1, 2, 3, \ldots \qquad \text{......}(2_0),$$

$$\nu_0 = \nu_e + [\omega_0'n' - \omega_0'x'n'^2] - [\omega_0''n'' - \omega_0''x''n''^2] \qquad \text{......}(3_0).$$

In every case where it has been possible to apply an adequate test, the new mechanics has been found to represent the observational data more accurately. It is therefore reasonable to extend its use to cases where no test is possible and the older theory might serve equally well.

For our present purpose it will suffice to use the approximate form $F(j) \doteqdot Bm^2$ first given in the older quantum theory.

The electronic transition $E_e' \rightarrow E_e''$ is accompanied by a change in I as well as of ω_0, x and other molecular constants. Hence the wave number of the $m' \rightarrow m''$ line of the $n' \rightarrow n''$ band is given by

$$\begin{aligned}\nu &= \nu_e + \nu_n + (E_m' - E_m'')/hc \\ &= \nu_e + \nu_n + F'(j') - F''(j'') \doteqdot \nu_e + \nu_n + B'm'^2 - B''m''^2 \qquad \ldots\ldots(4).\end{aligned}$$

The change $j'' - j'$ is restricted to -1, 0, and $+1$, and the lines corresponding to each of these three values constitute a *branch* of the band, the branches being called the R or "positive," the Q or "zero" and the P or "negative" respectively. Putting $(m'' + 1)$, m'' and $(m'' - 1)$ in turn for m' in (4)*, we obtain rough expressions for the branches, namely,

$$\begin{aligned}\nu_R &\doteqdot \nu_e + \nu_n + B' + 2B'm'' + (B' - B'')\,m''^2 \\ \nu_Q &\doteqdot \nu_e + \nu_n \qquad\qquad\quad + (B' - B'')\,m''^2 \\ \nu_P &\doteqdot \nu_e + \nu_n + B' - 2B'm'' + (B' - B'')\,m''^2 \qquad \ldots\ldots(5).\end{aligned}$$

If m'' is plotted against ν_R, ν_Q, and ν_P, i.e. in a Fortrat diagram, a parabola is obtained in each case with its axis parallel to the ν axis, the vertices being given by

$$\begin{aligned}m''_{R\text{ head}} &\doteqdot B'/(B'' - B'); \quad \nu_{R\text{ head}} \doteqdot \nu_e + \nu_n + B'B''/(B'' - B') \\ m''_{Q\text{ head}} &\doteqdot 0 \qquad\qquad\quad\;\; ; \quad \nu_{Q\text{ head}} \doteqdot \nu_e + \nu_n \\ m''_{P\text{ head}} &\doteqdot B'/(B' - B''); \quad \nu_{P\text{ head}} \doteqdot \nu_e + \nu_n - B'B''/(B' - B'') \ldots\ldots(6).\end{aligned}$$

Now if there is a decrease in I during the emission, i.e. $I' > I''$ and $B' < B''$, $m''_{R\text{ head}}$ is positive and $m''_{P\text{ head}}$ negative; thus the successive R lines of increasing m'' become closer together as they recede from the band-origin $(\nu_0 = \nu_e + \nu_n)$ towards higher ν, form a head at about $B'B''/(B'' - B')$ cm.$^{-1}$ above ν_0, and then gradually become wider apart with diminishing ν and still increasing m''; the P lines of increasing m'' do not form a head, but slowly become wider apart as they recede from ν_0 in the direction of lower ν; the Q branch, which is present in the bands of some, but not all, systems, *starts* with a head very near to ν_0 and runs away from the R head. Such a band degrades from its R and Q heads towards the infra-red.

If, on the other hand, there is an increase in I during the emission, i.e. $I' < I''$ and $B' > B''$, $m''_{P\text{ head}}$ is positive and $m''_{R\text{ head}}$ negative; the P lines now form a head at about $B'B''/(B' - B'')$ cm.$^{-1}$ below ν_0, the R lines now widen out without forming a head, and the Q lines again start with a head near ν_0 but now run away from the P head. Such a band degrades from P and Q heads towards the ultra-violet.

We must omit discussions of the intensities of the lines in the branches, the missing lines near the origin, perturbations, the application of the combination principle, and the types of doublets and triplets arising from certain physical causes; important as these all are for the rotational quantum analysis of the bands and for the recognition of the types and multiplicities of the initial and final electronic levels.

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* Strictly this should not be done, since generally m does not change by integral values as j does.

For each electronic state of the molecule the moment of inertia increases with the vibrational energy in a way expressed by

$$B'_{n'} = B'_0 - \alpha'(n' + \tfrac{1}{2}); \quad B''_{n''} = B''_0 - \alpha''(n'' + \tfrac{1}{2}) \qquad \ldots\ldots(7),$$

where α' and α'' are positive constants for the upper and lower electronic states. (For the sake of brevity the suffixes n' and n'' have been omitted from I', B' and I'', B'' in the above discussion). Hence the interval $B'_{n'} B''_{n''}$ $(B''_{n'} - B'_{n'})$ between the R or P head and the band-origin or the Q head varies from band to band throughout the system, and, while formula (3) for the band-origins approximately represents the Q heads, it must be modified in order to represent the R and P heads, thus

$$\nu_{\text{head}} = (\nu_e + \kappa) + [a'(n' + \tfrac{1}{2}) - b'(n' + \tfrac{1}{2})^2] \\ - [a''(n'' + \tfrac{1}{2}) - b''(n'' + \tfrac{1}{2})^2] + \theta(n' + \tfrac{1}{2})(n'' + \tfrac{1}{2}) \qquad \ldots(8).$$

The constant κ is positive for R and negative for P heads, and the coefficients a', b', a'', b'' differ appreciably from the corresponding coefficients in (3). Low dispersion data for band-heads do not often permit of the evaluation of the coefficient θ, in which case the $(n' + \frac{1}{2})(n'' + \frac{1}{2})$ term is omitted.

Bands for which n' (or n'') is constant and n'' (or n') varies constitute an n'' (or n') *progression*; thus the bands for which n', n'' are respectively 0,0 , 0,1 , 0,2 , 0,3... form the n'' progression $n' = 0$, and the 0,2 , 1,2 , 2,2 , 3,2... bands form the n' progression $n'' = 2$. Bands for which the change $n'' - n'$ is constant form a *sequence*; thus the $n'' - n' = +1$ sequence consists of the 0,1 , 1,2 , 2,3 , 3,4... bands. In analysing a system it is usually expedient to arrange the wave numbers of the heads in a table such that the 0,0 band appears in, say, the left-hand top corner, each n'' progression runs horizontally, each n' progression runs vertically and each sequence runs diagonally from top-left to bottom-right*. The vibrational quantum analysis may indeed be said to consist of the correct construction of such a table, for when this is achieved, the values of n' and n'' can be assigned with almost complete certainty, and the coefficients in equation (8) evaluated.

Criteria for the $n'n''$ assignments are:

(i) ν increases with decreasing n'' in an n'' progression and with increasing n' in an n' progression.

(ii) The intervals $\Delta\nu$ between successive bands of a progression decrease with increasing n' or increasing n'', very nearly in arithmetical progression if Q heads or band-origins are tabulated, and less nearly in arithmetical progression if R or P heads are used.

(iii) A decrease of I is accompanied by an increase of ω_0, and *vice versa*; hence, if the bands degrade towards the infra-red, $I'' < I'$, $\omega_0'' > \omega_0'$, and above the intervals $\Delta\nu$ are larger in an n'' progression than in an n' progression; the reverse is true if the bands degrade towards the ultra-violet.

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* Table 3 on p. 524 is an example, the perusal of which will help to make clear the present statements; it is, however, a composite table in which, for economy of space, R head data appear immediately above Q head data for a rather extensive band-system.

(iv) As a consequence of (i) and (iii), along a sequence n' and n'' increase in the direction in which the bands degrade.

(v) When the directions of increase of n' and n'' are thus settled, their values are decided by the sudden cessation of an n'' progression (say $n' = 0$ or 1) at its low-ν end, and of an n' progression (say $n'' = 0$ or 1) at its high-ν end; the test is applied by verification of the entire absence from the spectrogram of bands whose $\nu\nu$ are obtained by extrapolations beyond the top row and left-hand columns of the above table.

(vi) If the bands have measurable Q heads, in bands degraded to the red the interval $\nu_{R\,\mathrm{head}} - \nu_{Q\,\mathrm{head}}$ increases with diminishing n' along an n' progression and with increasing n'' along an n'' progression, and in bands degraded to the violet $\nu_{Q\,\mathrm{head}} - \nu_{P\,\mathrm{head}}$ *decreases* in these directions. These facts, which follow from equations (6) and (7), are more useful in the recognition of Q heads than as evidence for the n', n'' assignment.

(vii) The distribution of intensity amongst the bands of a system is normally of the type in which a progression (say $n' = 4$ or $n'' = 4$) has two intensity maxima separated by a minimum, and the locus of all the maxima is a curve of nearly parabolic form (the Franck-Condon parabola) such that (*a*) its axis approximately coincides with the 0 sequence, and represents a rapid decline of intensity from a maximum to zero; (*b*) if the change $I'' - I'$ or $\omega_0'' - \omega_0'$ is very small, its vertex coincides with the 0, 0 band (which is the strongest of the system), and its two limbs are close to one another and to the 0 sequence (which is the strongest, if not the only, sequence present); (*c*) as the change $I'' - I'$ or $\omega_0'' - \omega_0'$ increases, the vertex of the curve recedes from the 0, 0 band, and the limbs of the curve become wider apart; thus the wide curve of maxima which characterises a large change cuts the 0 sequence not at the 0, 0 band, but at a higher n', n'' band.

(viii) The vibrational isotope effect, if present and precisely measurable, furnishes an absolute check on the n', n'' numeration and is, in fact, the experimental evidence for the use of $(n + \frac{1}{2})$ instead of n in the vibrational energy terms in equations (2), (3) and (8).

As a result of the analysis of different band-systems of the same molecule, and as a demonstration of the Ritz combination principle as applied to band spectra, it is frequently found that a given electronic level (recognised usually by its associated vibrational energies, and less often by the moment of inertia I_0 and internuclear distance r_0 for that state) is involved in two or more systems, either as a common initial state, or as a common final state, or as the initial state for one system and the final for another. Thus, in the "red" and "violet" systems of CN, the band-origin equations (3) have common values of ω_0'' and $\omega_0''x''$, indicating that the final electronic state for each system has a common set of vibrational energy levels. In the spectrum of CO there are about nine systems involving only eleven electronic states, the final state for the visible Ångström system, for instance, being both the initial state for the extensive ultra-violet "4th positive" system and also the final state for another system; while for CO^+ (as also for $B^{11}O$ and $B^{10}O$) there are three known systems with only three electronic states. In spectra containing many known systems, e.g. H_2 and He_2, the system-origins form *series* of the Rydberg-Ritz type already well known in atomic line spectra.

A certain correspondence exists between the spectra and electronic states of many of the lighter molecules and those of the atoms containing two less extranuclear electrons, and it is inferred that in the molecule each atom retains its own *K* electrons, while the remaining electrons form an outer configuration similar to that in the comparable atom. Thus corresponding to the 11-electron atom Na, which has 2 *K*, 8 *L* and 1 *M* electrons, each of the 13-electron molecules BeF, BO, CN, CO^+, N_2^+ contains, besides its 2 + 2 *K* electrons, 9 outer electrons which are regarded as an outer structure of a group of 8 electrons, together with 1 outermost or valence electron. Similarly, the 21-electron molecules MgF, AlO, SiN, have, like the 19-electron atom K, 8 + 8 + 1 electrons outside the *K* electrons and the nuclei, and are thus also "one-valence-electron" molecules. Again, CO and N_2 (14 electrons) are, by comparison with Mg (12), "two-valence-electron" molecules*.

Aided by this correspondence, detailed theoretical study of the fine structure of bands of different types has led to the classification of molecular electronic levels into singlet, doublet, triplet,... levels, and into types which are to some extent analogous to the term-types S, P, D, F already known in atomic spectra. As in the case of atoms, the electronic levels of odd and even molecules have even and odd multiplicities respectively. The molecular electronic levels were until recently designated by the same capital letters, but it is sometimes necessary to discuss the electronic levels of molecules in relation to those of their constituent atoms, and to avoid confusion the above letters are now reserved for atomic levels, and Σ, Π, Δ, Φ are used for molecular levels.

This new notation also serves to emphasise the fact that the electronic levels in the two cases are not completely analogous. While transitions between similar states, e.g. $S \rightarrow S$, $P \rightarrow P$, are never found in atomic spectra, such transitions as $\Sigma \rightarrow \Sigma$, $\Pi \rightarrow \Pi$, are frequently represented in molecular spectra. Thus, the normal and lowest two excited states are ^2S, ^2P, ^2S respectively for Na (11) and K (19), and $^2\Sigma$, $^2\Pi$, $^2\Sigma$ respectively for the 13-electron and 21-electron molecules already mentioned; and in the CN spectrum, for instance, the "red" system is attributed to the transition $^2\Pi \rightarrow {^2\Sigma}$, and corresponds to the Na yellow doublet $^2P \rightarrow {^2S}$, while the "violet" system is due to $^2\Sigma \rightarrow {^2\Sigma}$ (the final state being, as for the "red" system, the normal $^2\Sigma$ state) and has no corresponding line $^2S \rightarrow {^2S}$ in the Na spectrum. Again, three band-systems which are well known in laboratory and stellar spectroscopy, namely, the "2nd positive" of N_2, the Swan system of C_2 and the blue-green (Antarian) system of TiO, are each attributed to a transition $^3\Pi \rightarrow {^3\Pi}$, which has no counterpart $^3P \rightarrow {^3P}$ in atomic spectra.

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* A note on heavier oxides and their comparable atoms appears in a footnote on p. 531, *q.v.*

DISCUSSION

Mr J. H. Awbery: I should like to thank Dr Jevons for his very clear introduction to the general subject of band spectra. I think I must be expressing the opinions of many others when I say that I am interested generally in "modern physics," although my active work lies in other directions; for those in this position there have been ample opportunities to read about the results and ideas of line spectroscopy, but our knowledge of band spectra has been limited to the facts that these spectra have been found to exhibit regularities, and that moments of inertia of the molecules could be estimated by means of them. The literature of the subject is very technical, and without some such survey as Dr Jevons has now provided, we lacked that substratum of knowledge which was necessary before more detailed accounts could be profitably studied. I should like to know more of the calculation of the function by which the rotational energy of the molecule is expressed in terms of the quantum number j. The forms quoted are identical with those obtained for the free rotator*, and it is stated that much more complicated forms are sometimes necessary. I suppose this refers, at any rate in part, to the fact that a molecule does not consist of two mass-points only. In terms of Bohr's picture, there may be orbits of various degrees of eccentricity, and these would make the simple expressions inapplicable. Perhaps Dr Jevons would correct me if this is wrong, and also give a few references either to summaries or to the most important papers which would enable me, and others in the same stages of ignorance, to lighten our darkness.

Author's reply: In my brief outline I have made no attempt to indicate methods of determining the rotational energy expression from the fine structure analysis of the bands. For such information I would refer Mr Awbery to the National Research Council's *Bulletin* no. 57 on "Molecular Spectra in Gases," pp. 142–177. The rotational energy expression $Bj(j+1)$ of the new mechanics was obtained and developed by Dennison, *Phys. Rev.* **28**, 318 (1926), Kronig and Rabi, *Nature*, **118**, 805 (1926), and *Phys. Rev.* **29**, 262 (1927), and Reiche, *Z. f. Phys.* **39**, 444 (1926).

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* For example, by Schrodinger: *Collected Papers on Wave Mechanics*, p. 35.

THE RELATION BETWEEN HYDROGEN PRESSURE AND FILAMENT RESISTANCE IN A TUBE CONTAINING GLOWING TUNGSTEN

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Read and discussed June 28, 1929

ABSTRACT. When a tungsten filament in a tube containing hydrogen is caused to glow, the gas rapidly disappears while the resistance of the filament rises progressively. The latter phenomenon can be used to measure the pressure of the hydrogen. It is suggested that chemical action takes place between the hydrogen and tungsten.

§ 1. INTRODUCTORY

In the course of preliminary experiments begun some time ago on the thermionic emission of tungsten in an atmosphere of hydrogen, it was found difficult to carry out accurate measurements, owing to the rapid disappearance of hydrogen in the tube. At the same time it was noted that the resistance of the filament increased. It was thought that this effect was probably due to lessened conduction and convection through the film of gas, and that the increase of resistance might be used to measure the pressure of the hydrogen, somewhat after the manner of the Pirani-Hale gauge, in which, however, wires are used at a much lower temperature.

In § 2 of this paper it is shown that the variations of the resistance of an electrically heated tungsten filament, glowing at high temperature in an atmosphere of hydrogen, can be used as a measure of the pressure of the hydrogen in the tube. In § 3 this method is applied to observations on the disappearance of hydrogen in the thermionic tube.

§ 2. RELATION BETWEEN FILAMENT RESISTANCE AND HYDROGEN PRESSURE

Theory. In the case of an electrically heated tungsten filament in an atmosphere of hydrogen the rate of loss of energy is equal to the input in watts, on the assumption that a steady state has been reached and that the loss of heat through the ends is negligible.

The heat is lost in two ways*:

(i) By radiation. The radiating power $\propto T^{\omega}$, where ω is a constant, taken as 4. The loss therefore $= \sigma(T^4 - T_0^4)$, where T and T_0 are the absolute temperatures of the surface and surroundings and σ is a constant.

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* It is assumed that at the temperatures (namely 1300° and 1800° absolute) and pressures dealt with in these experiments the loss of heat caused by the dissociation of the hydrogen into atoms can be neglected compared with the conduction, convection and radiation losses.

(ii) By conduction and convection through the film of gas. When a stationary film of gas is in contact with any hot object at high temperatures, free convection consists essentially of conduction through the film and can be calculated by the laws of conduction. Therefore if two surfaces at an infinitely small distance apart dx differ in temperature by dT, the rate of loss of heat,

$$Q = KA\, dt/dx,$$

where K is the thermal conductivity of the medium, between the surfaces, and A the area. Hence, for isothermal surfaces at a finite distance apart,

$$Q = \int K\,dT \Big/ \int \frac{dx}{A}.$$

Taking the conductivity K as a known function of the temperature, the value of $\int K\,dT$ becomes the product of the conductivity for the mean temperature of the surfaces and the temperature difference between them.

Let the space factor $1 \Big/ \int \frac{dx}{A}$ be denoted by s. If the wire and the surrounding film of gas be considered as a cylinder and cylindrical shell, the space factor

$$s = 2\pi l/\log_e (b/a),$$

where a and b are the internal and external radii of the film and l is the length.

Therefore if T is the temperature of the wire, and T_0 the temperature at the outer surface of the film, the loss W in watts per unit length

$$= \frac{2\pi \times 4{\cdot}2}{\log_e (b/a)} \int_{T_0}^{T} K\,dT.$$

Since s, the space factor per unit length, $= 2\pi/\log_e (b/a)$, the watts lost per unit length by conduction and convection $= s\,(\Phi_1 - \Phi_2)$, where

$$\Phi_1 = 4{\cdot}2KT,$$

and

$$\Phi_2 = 4{\cdot}2KT_0.$$

The watts lost per unit length by radiation

$$= \sigma\pi a\,(T^4 - T_0^4),$$

and the watts input per unit length

$$= RI^2/l,$$

where I denotes current in the wire.

Assume that T_0^4 and $s\Phi_2$ can be neglected compared with the T terms, and to a first approximation let k be the average value of $4{\cdot}2\,K$.

Then

$$RI^2/l = \sigma\pi a T^4 + s\Phi_1.$$

Taking the resistance to be approximately proportional to the absolute temperature, let $T = CR$, where C is a constant.

Then

$$RI^2/l = \sigma\pi a C^4 R^4 + skCR,$$

$$I^2/l = \sigma C^4 R^3 \pi a + skC \qquad \text{......(1).}$$

Let R_0 be the resistance when the pressure is 0, and there are no conduction or convection losses through the film of gas.

Then
$$R_0 I^2/l = \sigma\pi a C^4 R_0^4,$$
$$I^2/\sigma\pi a l C^4 = R_0^3 \qquad \text{......(2).}$$

From (1)
$$(I^2/l - skC)/\sigma\pi a l C^4 = R^3 = (R_0 + \Delta R)^3,$$
where
$$\Delta R = \partial R/\partial P . \Delta P.$$

Hence
$$(I^2 - slkC)/\sigma\pi a l C^4 = R_0^3 + 3R_0^2 \Delta R + \dots$$
or
$$- slkC/\sigma\pi a l C^4 = 3R_0^2 \Delta R \qquad \text{......(3),}$$
terms in ΔR^2 and ΔR^3 being neglected.

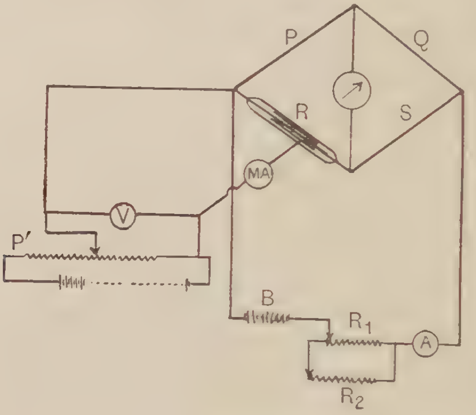

Fig. 1. Circuit diagram.

P, Q, R, S, arms of Wheatstone bridge; B, battery in bridge circuit for heating current; R_1, R_2, resistances, large and small, placed in parallel for final adjustment of current; P′, high resistance rheostat with dry battery of 120 volts; V, voltmeter; MA, microammeter.

Divide (3) by (2), so that
$$- slkC/3I^2 = \Delta R/R_0,$$
on the assumption that k is independent of the pressure, and that s is constant for equal increases of pressure.

Then
$$\Delta R/R_0 \propto 1/I^2,$$
or
$$\Delta R/R_0 \times I^2 = K,$$
where K is a constant.

Method of investigation. The tube used in the experiments was a diode, cylindrical in shape. A tungsten filament, welded to thick leads, was stretched along the axis of a cylindrical copper anode. The dimensions were:

Length of tungsten filament	...	7·5 cm.
Diameter of tungsten filament	...	0·012 cm.
Length of anode cylinder ...	...	20 cm.
Diameter of anode cylinder ...	...	2 cm.

The tube was connected to (1) a Geissler tube, (2) a liquid air trap, (3) an H_2So_4 gauge, in which pressures could be read to ·1 mm. of H_2So_4 (= ·014 mm. of mercury) by means of a travelling microscope, (4) a tube containing coco-nut charcoal for immersing in liquid air, (5) a Geryk pump for preliminary evacuation of the apparatus. The apparatus was placed in an oven and the occluded gas baked out by preliminary and prolonged pumping and heating. The hydrogen was introduced through a heated palladium tube.

Electrical arrangements. The filament R and a compensating low resistance S were placed in the adjacent arms of a Wheatstone bridge. The arrangement of apparatus is shown in Fig. 1. The arm Q was 2000 ohms, and P varied with R.

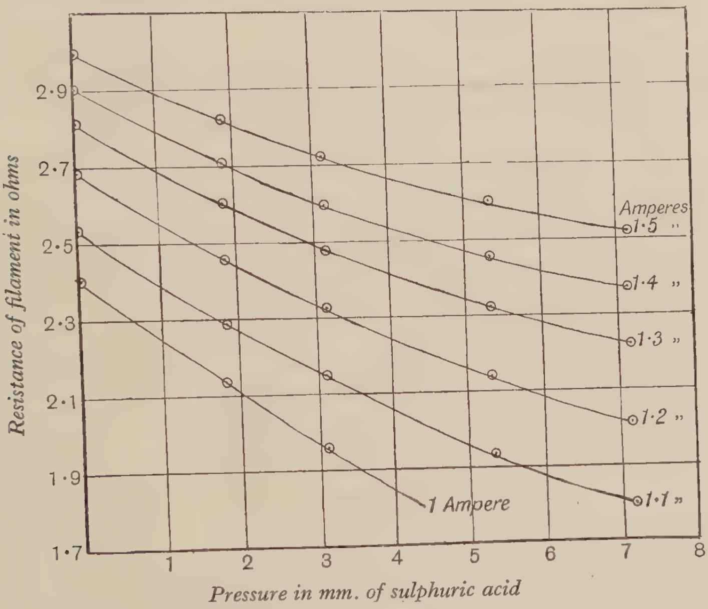

Fig. 2. Typical series of resistance-pressure curves for varying values of the heating current.

Results. Fig. 2 shows a typical series of resistance/pressure curves. There were many series taken, with four filaments, and in every case the permanent increase in resistance was noted, though the value of $\Delta R/R_0$ for equal increases of pressure did not alter for a constant heating current. Values of $\Delta R/R_0$ for equal increases of pressure Δp are given below for varying values of the heating current, the values of $\Delta R/R_0$ being calculated from series of graphs of which Fig. 2 is an example.

I	1·5	1·4	1·3	1·2	1·1
$\Delta R/R_0$	0·045	0·054	0·061	0·072	0·082
	0·056	0·049	0·081	0·09	0·096
	0·042	0·061	0·052	0·072	0·092
	0·058	0·07	0·069	0·076	0·09
	0·045	0·056	0·07	0·073	0·087
	0·048	0·051	0·06	0·07	0·091
	0·062	0·066	0·06	0·069	0·09
	0·058	0·061	0·077	0·082	0·092
Mean	0·052	0·059	0·066	0·076	0·091

Fig. 3 gives the values of $\Delta R/R_0$ plotted against $1/I^2$, showing that $\Delta R/R_0 = K/I^2$, from which $K = 0{\cdot}107$.

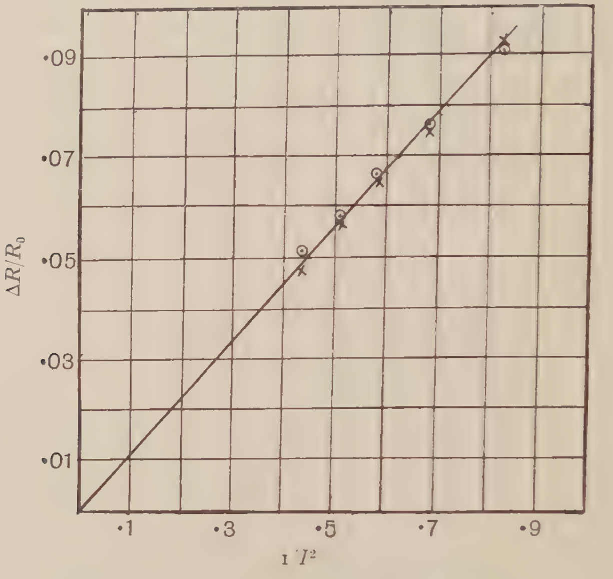

Fig. 3. Relation between resistance increments and the heating current. Calculated × × ×. Observed ○ ○ ○.

§3. OBSERVATIONS ON THE DISAPPEARANCE OF HYDROGEN IN THE THERMIONIC TUBE

The disappearance of gas in the discharge tube has been studied extensively, and this effect was very marked in the type of tube used for these experiments. It was therefore thought that the tungsten filament glowing at a high temperature in an atmosphere of hydrogen could itself be used as a pressure gauge of the Pirani-Hale type, as described in § 2. This method was chosen because it was necessary to keep the heating current constant for the purposes of the measurement of the electronic emission.

Many attempts were made to get satisfactory and consistent readings of the thermionic currents, at various pressures, when the voltage applied between filament and anode was slowly increased. The difficulties that were encountered suggested this part of the investigation, in which the rate of increase of resistance of the filament, owing to the diminished cooling effect due to the disappearance of hydrogen, could be used as an indication of the pressure. This method would do away with the necessity for any other type of gauge, which would be an advantage when it is advisable to avoid any trace of the mercury vapour from a McLeod gauge.

It was carefully observed that: (i) There was no increase of resistance of the filament with time at high temperatures, before the introduction of the hydrogen, or after the total disappearance of the hydrogen. (ii) The pressure of the hydrogen in the tube remained constant if the filament was not glowing brightly. (iii) The application of a potential difference between filament and anode did not alter the rates of increase of resistance of the filament, or of the disappearance of the hydrogen.

The gradual permanent increase in the resistance of the filament, which in the experiment was from ·62 to ·92 ohm, is shown in both parts, and it is suggested in the discussion that there may be chemical action between the hydrogen and the hot tungsten.

Experimental procedure. The thermionic tube was similar to that used in § 2, while the electrical arrangements were slightly modified by the introduction of a rotating electrically driven commutator. This was arranged in such a way that there was no heating current flowing in the circuit when a voltage was applied between filament and anode. This was done to avoid the effects due to the drop of potential along the wire, the current and the application of the voltage between filament and anode being alternately intermittent. Hydrogen was introduced into the apparatus by heating the palladium tube, and the heating current was then increased till the filament was glowing brightly.

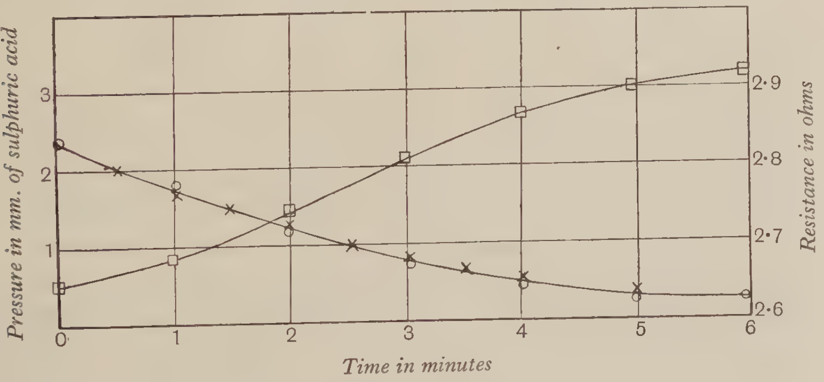

Fig. 4. Observed values of pressures O——O——O.
Calculated values of pressure ×——×——×.
Resistance of filament □——□——□.

The temperatures given were deduced from the change of resistance of the filament by the use of data given by Langmuir (1).

Alternate readings were then taken of the resistance of the filament and the pressure of the hydrogen as shown on the sulphuric acid gauge.

It is shown in § 2 that $I^2\Delta R/R_0 = K$, where $K = \cdot 107$. Thus for any experimental readings of $\Delta R/R_0$ for a known value of I^2, Δp can be calculated. Values of p were therefore deduced for any given value of the resistance of the filament.

Fig. 4 shows the increase of resistance with time, and the same figure shows the values of the pressure as observed on the sulphuric acid gauge together with those calculated as above. These are found to be in good agreement. This is shown more clearly in Fig. 5, where the results are recorded as resistance/pressure curves.

It is therefore concluded that the method proposed for estimating the hydrogen pressure by observations of the filament resistance is, for the small range of pressures studied, satisfactory.

§ 4. DISCUSSION OF RESULTS

It has been shown that a measurement of the pressure of a gas in a thermionic tube containing a tungsten filament can be made from direct observations of the resistance of the filament, if the latter is heated to high temperatures in an atmosphere of hydrogen. This method is independent of the gradual permanent increase of the resistance of the filament, so that there is no necessity for repeated calibrations of the pressure gauge.

The permanent increase may be due to the sputtering of the cathode, to the action of traces of water vapour, or to some chemical action between the heated tungsten and the hydrogen. Calculations showed that the increase was too great to be accounted for by cathodic sputtering, and care was taken to avoid the effects of any traces of water vapour. This was done by the alternate heating and cooling by liquid air of the tube containing charcoal, which was placed between the thermionic tube and the sulphuric acid gauge. The third of the foregoing explanations was suggested because of the rapid disappearance of the hydrogen when the filament was raised to a high temperature, whereas little or no effect was observed when the filament was not glowing.

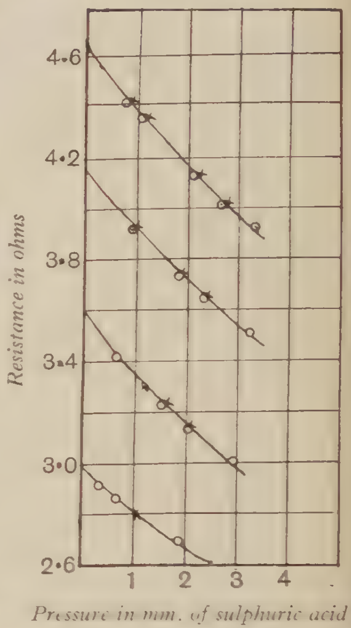

Fig. 5. Calculated and observed values shown as resistance pressure curves.

In support of the suggestion that there was a chemical action, the following rough calculation is given of the total masses of tungsten and hydrogen disappearing in the course of the experiment:

Initial mass of filament = 0·02 gm.
Final mass of filament = 0·014 gm.
Loss in mass = 0·006 gm. = m_1.
Loss in mass of hydrogen = 0·000063 gm. = m_2.

(Calculated from volume of vessel and gas laws.)

Therefore m_1/m_2 = (mass of tungsten)/(mass of hydrogen) = 97/1.

This approximation suggests that there may be chemical action between the tungsten (atomic weight 184) and hydrogen, a compound with empirical formula H_2W being formed.

Investigations on the disintegration of a tungsten cathode in an atmosphere of hydrogen have however shown (2) that it is small compared with that which occurs in other gases, and is anomalous; while Dushman (3) states that investigators have observed that hydrogen is absorbed by tungsten to a negligible extent.

Stead and Trevelyan (4) suggest that hydrogen acts on the filament to form an endothermic compound stable at high temperatures, and the General Electric Co. Research Staff (5) show that if hydrogen is present it should disappear in the presence of hot tungsten without ionisation by a field.

Langmuir (6), in his extensive work on the subject, showed that hydrogen would disappear even without the passage of a discharge. He found that hydrogen could be dissociated by tungsten and other metallic wires when the temperature of the metal was raised above 1300° absolute and that the disappearance is due to the dissociation of the hydrogen into atoms which condense on the walls, but that the observed decrease of pressure corresponds only to 1/7 or less of the amount actually dissociated. There is a marked increase above 2500° absolute.

Congdon (7) mentions the peculiar behaviour of hot tungsten in the presence of hydrogen. It is noteworthy that many experimenters, when working with hydrogen, avoid the use of a tungsten cathode.

§ 5. SUMMARY OF CONCLUSIONS

It has been shown in this paper:

(i) That in an electrical manometer, if the heating current is kept constant the relative diminution of resistance with pressure varies as the square of the heating current.

(ii) That this principle may be applied to the deduction of values of the pressure of hydrogen in a tube, by readings of the resistance of the tungsten filament, which increases owing to the disappearance of the hydrogen.

(iii) That the permanent increase of the resistance may be due to the action of the hydrogen on the hot tungsten.

§ 6. ACKNOWLEDGMENTS

In conclusion I should like to express my thanks to Professor Richardson for his helpful criticism and advice and for allowing me to work in his laboratories. I should also like to thank Dr W. A. Leyshon for her help and constructive suggestions.

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(2) *Phil. Mag.* G.E.C. Staff, **45**, 98 (1923).
(3) Dushman, "High Vacuum. Theory of Adsorption at Low Pressures."
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(5) *Trans. Faraday Soc.* G.E.C. Staff, **17**, 485 (1922).
(6) *Journ. American Chem. Soc.* **37**, 1161 (1915).
(7) *Phil. Mag.* **47**, 458 (1924).

DISCUSSION

Mr N. L. Harris: While congratulating the author upon the results she has obtained by using this method of pressure measurement, I suggest that some modifications should be made in designing a practical gauge on these lines. The temperature scale of tungsten has been revised several times since 1912, with corresponding revision of its specific properties as functions of temperature: the latest and most complete information is to be found in that given by Jones and Langmuir*. It is not clear (p. 547) that $s\Phi_2$ is negligible compared with $s\Phi_1$. Over the range of temperature used, the expression $T = CR$ should be replaced by $T = 3{\cdot}24 . 10^7 \rho \times 192$, where ρ is the resistivity of tungsten in ohm cm. At 1500° the constant term amounts to some 15 per cent. of the whole and must then enter the equations in the fourth power, with the possibility that even over small temperature ranges the end expression in ΔR may need modification. A filament as thick as 0·012 cm. in diameter and only 7·5 cm. long suffers badly from "end effects" when running at 1500°, in fact only a central few millimetres are at a uniform temperature†. The entry of gas into the tube will modify the temperature distribution and change the overall resistance apart from the main effect we are studying. Unless the "ends" are short to start with, the effect may be serious: I suggest wire about 0·0025 cm. in diameter as more suitable. Again, traces of oxidising vapours may change the thermal emissivity of the wire by large amounts as surface oxide layers form, and vapours of hydrocarbons are capable of carbonising the tungsten at 1600°‡. In both cases the change in resistance of the wire for constant heating current may be large. A trace of water vapour or carbon dioxide thins a hot tungsten wire considerably in cyclic reactions. Perhaps the presence of the tap between the liquid air trap and the hot filament, in the apparatus described, accounts in these ways for some of the effects mentioned in the latter part of the paper.

Dr M. C. Johnson: Some time ago I had occasion to consider the relative magnitude, under certain conditions, of the various factors contributing to this change of resistance of a hot tungsten wire in hydrogen. The classification of a few of these factors may be of interest to those reading the paper, to which all workers *in vacuo* are indebted for its careful and thoroughgoing attainment of consistency in a very complex problem.

1. *Changes of resistance due to cooling of wire by gas.* (*a*) Change in composition of gas mixture whose components are differentially conducting. (I should like to be assured that this is negligible in the present work. The partial pressure of H_1 in the H_2 must be considerable when emission is going on at certain pressures.) (*b*) Diffusion away from the wire of H_1 capable of giving up heat of recombination. (Did the author find any trace of this at her highest temperatures?) (*c*) Simple change of total pressure.

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* *General Electric Review*, **30**, 310 (1927). † Worthing, *Journ. Frank. Inst.* **194**, 597 (1922).

‡ Andrews, *Journ. Phys. Chem.* **27**, 270 (1923).

2. *Changes of resistance due to altered composition of wire.* If the wire were not initially free from oxide this would gradually disappear in the hydrogen. The author has carefully eliminated water vapour: would this act simply by oxidation, if present? Her deduction of a definite compound $(H_2W)_x$ is an important advance on the usual vague assumption that these substances do not react. Will this reaction reverse at the highest temperatures? Is there any sign of solution of the hydrogen in the tungsten?

3. *Changes of resistance due to liberation of heat at gas-solid interface.* Any H_1 dissociated by electron impact may communicate 10^5 cal./gm.-mol. in catalytic recombination at the tungsten surface. Cold tungsten wires can be made white hot by insertion in a stream of partially dissociated H. I have had occasion to wonder before whether this, or the heat of adsorption (which I think can reach 10^4 cal.), will not affect resistance considerably. Presumably there is some temperature at which the Langmuir cooling effect is balanced by such heating effects. Can the author give any advice as to this?

I should also be grateful if the author can give any advice as to whether it is possible to know—from "fatigue" effects for example—how much of the "lost" hydrogen goes to the tungsten and how much to the glass walls.

Author's reply: I should like to thank Mr Harris and Dr Johnson for their criticisms and suggestions, but should point out that the method of pressure measurement described in my paper is not recommended as a practical form of gauge. I felt that the point of interest was the fact that, during a long course of experiments, it was possible to make simple and accurate estimations of the pressure of hydrogen by the variations in the electrical resistance of the tungsten filament, even though chemical changes might be taking place. If the object had been to design a practical form of gauge a shorter wire of smaller diameter would have been used to avoid the irregularity of temperature distribution and the end losses. It was not necessary, for the purposes of the experiment, to have an exact knowledge of the temperature, and the values given were calculated from Langmuir's original tables merely to indicate the range of temperature through which the filament was heated. It was assumed that, in general, $s\Phi_2$ could be neglected compared with $s\Phi_1$, if the filament were raised to a high temperature. The fourth power term applies to the radiation, and it is known that the heat lost in this way is small compared with the conduction and convection losses.

There is the possibility that any hydrocarbon vapour will react with incandescent tungsten to form tungsten carbides. A spectroscopic examination of the gas in the tube, however, showed only hydrogen lines and bands, though this could not be taken as a proof of the entire absence of carbon.

At the temperature given, it seems unlikely that the results would be affected by the loss of heat due to the change in the composition of the gas. It is well known that when a hot cathode is employed there will be only a slight amount of thermal dissociation of H, even with a wire operated at 2500° C. At the highest temperature used in my experiments the results showed none of those irregularities that would be consequent upon the abnormally highc onductivity brought about by the hydrogen atoms diffusing into the colder gas, and, on re-combining, giving up the heat of reaction.

I have had no opportunity of studying the problem from the chemical standpoint and cannot, therefore, give any information on this subject, though it seems probable that the heat of adsorption would affect the resistance. It was not possible to find out how much of the lost gas went to the walls, and how much to the filament. I assumed in my approximate calculation that all the gas which disappeared combined with the tungsten. There was no darkening of the glass of the tube, nor was there any return of pressure after the hydrogen had disappeared.

All the effects that have been mentioned may play a part in the variation of the resistance, yet the facility and accuracy with which I was able to calculate the pressure led me to suggest that the simple explanation which I have offered seems justified by the consistent results of repeated experiments.

THE BAND SYSTEMS OF TITANIUM OXIDE

By FRANCES LOWATER, Ph.D., F.R.A.S.

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ABSTRACT. (i) The bands of TiO have been found to extend toward the infra-red through some 800 Å further than the range previously known. (ii) Bands in the orange, red and infra-red regions have been analysed into two systems, distinct from the blue-green system. One of these is due to the transition $^1\Pi \rightarrow {}^1\Sigma$, the other to $^3\Sigma \rightarrow {}^3\Pi$, the latter having the same final energy level as the blue-green system $^3\Pi \rightarrow {}^3\Pi$. (iii) Analysis of other bands in the red is in progress.

§ 1. INTRODUCTION

In 1904 and 1907 Prof. A. Fowler* published his investigations on the origin of the bands characteristic of the M-type stars and showed that they arose from an oxide of titanium; he photographed the spectrum and measured the heads, sub-heads and maxima of the bands from λ 4350 to λ 7200. Numerous investigations of these bands in their relation to stellar phenomena have appeared during many years, but little has yet been published on the analysis of their gross and fine structure†, ‡, §, ‖. The plate accompanying Prof. Fowler's second paper shows that all the bands are degraded toward the red, but it exhibits a distinct difference in structure between the bands in the region from the violet to green and those in the region from the orange to the infra-red. In 1922–1923 the author re-photographed the spectrum from λ 5950 to λ 4000 in the second order of the 10 ft. grating of the Imperial College of Science, the prime object at the time being the solution of a problem in stellar spectroscopy¶. By the use of an iron arc fed with titanium dioxide, it was found that the banded structure extended to about λ 4000, but had no well-defined heads of wave-length shorter than λ 4205. Publication of these spectrograms was postponed while analysis of the fine structure was in progress. In 1926 A. S. King**, using the electric furnace and passing a strong current of oxygen through a graphite tube containing titanium, also found that the banded structure extended to about λ 4025; with the aid of a registering microphotometer he determined the wave-lengths of ten maxima, most of which he considered to be probable band heads.

Birge and Christy having analysed three bands in the blue-green region, namely, the (1, 0), (0, 0) and (0, 1), investigation of the red and infra-red region seemed to be of next importance.

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* *Roy. Soc. Proc.* A, **73**, 219 (1904); **79**, 509 (1907).

† Fiebig, *Z. wiss. Phot.* **8**, 73 (1910).

‡ Eder and Valenta, *Wien. Ber.* **119**, 37 (1910).

§ Birge and Christy, *Phys. Rev.* **29**, 212 (1927), (abstract); *Nature*, **122**, 205 (1928).

‖ Christy, Thesis, in the press.

¶ Frost and Lowater, *Astrophys. J.* 58, 265 (1923).

** *Publ. Astron. Soc. Pac.* **38**, 173 (1926).

§ 2. EXPERIMENTAL PROCEDURE

The source used was a Pfund iron arc supplied with an extra radiator and fed with titanium dioxide. The spectrum was photographed by means of a spectrograph of the Littrow type, having a dense glass prism of 30°, of which the dispersion ranged from 8·6 Å/mm. at λ 5600 to 35·5 Å/mm. at λ 8700. Spectrograms were taken with sensitised kryptocyanine and neo-cyanine plates from λ 5500 to λ 8800; panchromatic plates were also used in order to obtain a truer estimate of the intensity of the bands by taking into account the sensitivity of the three kinds of plates.

Measurements of the heads were made in the usual manner, the wave-lengths being referred to those of iron lines recommended as secondaries by the International Astronomical Union* wherever available, otherwise to wave-lengths published by Meggers and Kiess†. The numerous titanium lines occurring in this region were identified by the table of wave-lengths of Ti given by H. N. Russell‡.

The wave-length of the least refrangible head determined with certainty is 7996 Å; that of the least refrangible head hitherto recorded is 7197 Å (Fowler). Thus the bands have been found to extend through 800 Å further into the infra-red than the range previously known. Although spectrograms were continued through still another 800 Å into the infra-red, only one other possible head could be detected after elimination of the atomic Ti lines included in Russell's table.

§ 3. INTENSITY AND MULTIPLICITY

At first the distribution of intensity appears unusual, but vibrational analysis reveals the explanation of this appearance. Further, it will be observed from the plate that some heads appear to be double, others triple; and where they are merely double, the second head is much less strong than the first. Such double heads have the appearance of R and Q heads, but the data obtained from the difference in their wave-numbers§ do not give decisive proof of this. However, the assignment of the electronic transitions arrived at by analogy with the "comparable atom" requires R and Q heads; this point will be more fully discussed in a later section.

Four sequences in the region between λ 6300 and λ 8000 form a system of triplets, the R heads of which may be denoted by R_a, R_b, R_c or a, b, c, and the Q's by Q_a, Q_b, Q_c; the differences in the wave-number of these triplet heads of the (0, 0) band are $R_a - R_b = 66{\cdot}6$, $R_b - R_c = 74{\cdot}4$ cm.$^{-1}$, while the R and Q separations are of the order of 11 cm.$^{-1}$. The appearance of the narrowly spaced triple heads is produced by the proximity of the second head of the first member of the triplet sequence to the first head of the third member of the triplet, as for instance the R_a head of the (1, 1) band to the R_c head of the (0, 0) band. In some cases such heads coincide and produce the effect of a distribution of intensity which appears quite anomalous.

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* *Trans. Int. Astr. Union*, **3**, Table 1 (1929).

† *Scientific Papers*, *Bur. Stan.* No. 479 (1924).

‡ *Astrophys. J.* **66**, 347 (1927).

§ Jevons, *Roy. Soc. Proc.* A, **117**, 351 (1928).

In addition to this triplet system, a singlet system has been found in the orange; so far as it has yet been determined, it consists of one sequence only with its (0, 0) head at λ 5597·85, ν 17859·1 cm.$^{-1}$. Here the $R - Q$ separations are of the order of 19 cm.$^{-1}$.

The analysis of some thirty to forty other heads, not included in the singlet or triplet systems mentioned above, nor in the less refrangible portion of the blue-green system, is in progress.

§ 4. OBSERVATIONAL DATA

In Table 1 are collected the data for the heads which have been found between λ 5599 and λ 8800, including some which belong to the blue-green system. Columns 1 and 2 contain the wave-lengths, intensities (in parentheses) and wave-numbers respectively. Column 3 contains the vibrational quantum numbers, with prefixed letters distinguishing the bands of different systems, and suffixed letters the members of the triplets: α indicates members of the blue-green system, identified by the formula of Birge and Christy; β the R and Q heads of the singlet orange system; heads designated by γ belong to the red-infra-red system. Suffixes a, b, c indicate the first, second and third members of the triplet heads in the red-infra-red and blue-green systems. Heads with no quantum numbers assigned have not yet been completely analysed. Column 4, $O - C$, contains the differences between the observed wave-numbers and those calculated from equations (1) and (1′) for the orange system β, from equation (2) for the red-infra-red system γ, and from Birge and Christy's formula for the blue-green system α. Column 5, $O - C$, contains similar differences found from equation (3) for system γ.

All the R and Q heads so far identified of the singlet orange system β are included in the first ten lines of Table 1; they are put into the form of n' and n'' progressions in Table 2 in order to exhibit the first differences between the members of the sequence. Since the system consists of a single (0) sequence only, no vibrational constants can be determined, but it can be represented by the following equation, where $n = n' = n''$ and these symbols have integral values 0, 1, 2 ...:

$$\nu = \nu_e + (\omega_0' - \omega_0'')(n + \tfrac{1}{2}) - (\omega_0'x' - \omega_0''x'')(n + \tfrac{1}{2})^2,$$

which becomes for the R and Q heads, respectively,

$$\nu_R = 17909{\cdot}04 - 99{\cdot}54\,(n + \tfrac{1}{2}) - 0{\cdot}302\,(n + \tfrac{1}{2})^2 \qquad \ldots\ldots(1),$$

$$\nu_Q = 17890{\cdot}06 - 99{\cdot}58\,(n + \tfrac{1}{2}) - 0{\cdot}257\,(n + \tfrac{1}{2})^2 \qquad \ldots\ldots(1').$$

The vibrational analysis of the bands in the red-infra-red system γ is shown in Tables 3 and 4, which consist of the usual n' and n'' progressions of R and Q heads respectively; they are arranged in triple form to demonstrate the consistency of the triplets. From the data in Table 3 equations (2) and (3) have been deduced, the coefficients of $(n' + \tfrac{1}{2})$ and $(n'' + \tfrac{1}{2})$ giving the vibrational frequency of the rotationless molecule in the initial and final states respectively.

Table 1. Heads of bands of TiO

λ (air)	ν (vac.)	n', n''	$O - C$	$O - C$
5597·85 (8)	17859·1	β (0, 0) R	−0·1	
5603·81 (3)	17840·1	β (0, 0) Q	−0·1	
5629·28 (7)	17759·3	β (1, 1) R	+0·3	
5635·27 (2)	17740·4	β (1, 1) Q	+0·3	
5661·55 (7)	17658·1	β (2, 2) R	−0·2	
5667·59 (2)	17639·3	β (2, 2) Q	−0·2	
5694·42 (4)	17556·2	β (3, 3) R	−0·7	
5700·61 (2)	17537·1	β (3, 3) Q	−1·3	
5727·43 (3)	17455·0	β (4, 4) R	0·0	
5733·40 (2)	17436·8	β (4, 4) Q	0·0	
5759·56 (4)	17357·6	α (0, 2) R_b	0·7	
5761·99 (6)	17350·3	α (0, 2) R_c	−0·8	
5811·16 (5)	17203·5	α (1, 3) R_b	−2·6	
5814·96 (6)	17192·2			
5863·01 (4)	17051·3	α (2, 4) R_b γ (7, 3) R_a	−2·5 +1·5	 +0·3
5870·56 (2)	17029·4			
5872·71 (2)	17023·2			
5904·86 (5)	16930·5			
5922·02 (5)	16881·5			
5926·06 (3)	16870·0			
5949·92 (3)	16802·3			
5954·64 (2)	16789·0			
5961·27 (1)	16770·3			
6006·48 (3)	16645·0			
6034·66 (1)	16566·4			
6051·02 (3)	16521·6			
6057·59 (2)	16503·6			
6064·70 (2)	16484·3	γ (4, 1) Q_b		
6148·79 (2)	16258·9	γ (5, 2) R_c	−0·8	+1·8
6159·26 (2)	16231·3	α (1, 4) R_b	−2·8	
6162·23 (2)	16223·4			
6174·55 (3)	16191·0			
6183·45 (2)	16167·7			
6186·64 (5)	16159·4			
6190·09 (3)	16150·4			
6215·24 (6)	16085·0	γ (6, 3) Q_c		
6222·37 (4)	16066·0			
6226·31 (3)	16056·4			
6268·31 (3)	15948·9	α (3, 6) R_a	0·5	
6275·44 (1)	15930·2	γ (8, 5) R_a	+2·1	+6·6
6321·66 (1)	15814·7	γ (2, 0) R_b	+0·3	+0·4
6334·82 (1)	15781·6			
6350·44 (1)	15743·1	γ (2, 0) R_c	+1·7	+3·4
6354·72 (1)	15732·6	γ (2, 0) Q_c		
6371·29 (1)	15691·9			
6382·91 (1)	15658·9	γ (3, 1) R_b	+0·2	+0·9
6399·56 (1)	15621·5	γ (9, 6) R_c	+1·6	−6·2
6414·19 (1)	15586·3	γ (3, 1) R_c	+1·1	+2·9
6447·78 (1)	15505·4	γ (4, 2) R_b	+0·9	+1·8
6479·02 (1)	15430·2	γ (4, 2) R_c	−0·1	+1·2
6483·64 (2)	15419·2	γ (4, 2) Q_c		
6510·84 (1)	15354·8			
6512·60 (1)	15350·6	γ (5, 3) R_b	−1·1	−0·6
6517·29 (1)	15339·6	γ (5, 3) Q_b		
6543·78 (1)	15276·6	γ (5, 3) R_c	−0·1	0·0
6551·44 (1)	15264·0	α (1, 5) R_c	−1·2	
6562·17 (1)	15234·7	α (8, 11) R_c	+2·6	
6579·01 (1)	15195·7			
6594·01 (1)	15161·1			
6626·08 (2)	15087·7	α (9, 12) R_a	−1·3	
6634·30 (2)	15069·0			
6651·46 (5)	15030·1	γ (1, 0) R_a	+1·5	+0·1
6657·73 (2)	15016·0	γ (1, 0) Q_a		
6681·06 (6)	14963·6	ν (1, 0) R_b	+0·3	+0·3
6685·97 (1)	14952·7	γ (1, 0) Q_b		
6691·21 (4)	14940·9	α (10, 13) R_b	−1·7	
6714·37 (6)	14889·4	γ (1, 0) R_c	−0·3	+0·7

λ (air)	ν (vac.)	n', n''	$O - C$	$O - C$
6719·32 (6)	14878·6	γ (1, 0) Q_c γ (2, 1) R_a	 − 0·3	 − 2·8
6723·95 (5)	14868·2	γ (2, 1) Q_a		
6747·80 (5)	14815·6	γ (2, 1) R_b	+ 0·3	+ 0·9
6751·81 (4)	14806·8	γ (2, 1) Q_b		
6756·30 (6)	14797·0	α (11, 14) R_b	− 2·1	
6781·93 (5)	14741·3	γ (2, 1) R_c	− 0·2	+ 0·9
6785·81 (4)	14732·6	γ (2, 1) Q_c γ (3, 2) R_a	 + 0·4	 + 2·1
6815·27 (5)	14669·1	γ (3, 2) R_b	+ 0·4	+ 1·1
6820·17 (3)	14658·5	γ (3, 2) Q_b		
6850·23 (5)	14594·0	γ (3, 2) R_c	− 0·6	+ 0·6
6852·33 (6)	14588·0	γ (4, 3) R_a	− 0·2	+ 1·8
6858·06 (4)	14577·5	γ (4, 3) Q_a		
6883·84 (3)	14522·8	γ (4, 3) R_b	− 0·8	+ 0·3
6919·55 (4)	14447·9	γ (4, 3) R_c γ (5, 4) R_a	− 1·1 + 0·7	− 0·6 + 1·1
6925·76 (2)	14435·0	γ (5, 4) Q_a		
6941·89 (1)	14401·4			
6988·51 (1)	14305·3	γ (5, 4) R_c	+ 0·6	− 0·2
7054·51 (8)	14171·4	γ (0, 0) R_a	0·0	0·0
7060·01 (3)	14160·4	γ (0, 0) Q_a		
7087·89 (12)	14104·7	γ (0, 0) R_b	0·0	0·0
7093·17 (4)	14094·0	γ (0, 0) Q_b		
7125·61 (14)	14030·1	γ (0, 0) R_c γ (1, 1) R_a	0·0 + 1·1	0·0 − 0·3
7131·34 (5)	14018·7	γ (0, 0) Q_c γ (1, 1) Q_a		
7159·03 (6)	13964·5	γ (1, 1) R_b	+ 0·2	+ 0·8
7164·31 (4)	13954·2	γ (1, 1) Q_b		
7171·22 (5)	13940·8	α (4, 9) R_b	− 0·8	
7183·00 (10)	13917·9			
7197·67 (8)	13889·6	γ (1, 1) R_c γ (2, 2) R_a	− 0·2 0·0	− 1·7 + 0·5
7203·64 (4)	13878·1	γ (2, 2) Q_a		
7219·40 (6)	13847·8	γ (1, 1) Q_c		
7230·44 (4)	13825·1	γ (2, 2) R_b	− 0·2	+ 0·5
7269·05 (6)	13752·6	γ (2, 2) R_c γ (3, 3) R_a	+ 1·7 − 0·4	+ 2·6 − 1·5
7273·93 (5)	13743·9	γ (2, 2) Q_c γ (3, 3) Q_a		
7290·80 (5)	13712·1			
7297·01 (3)	13700·4			
7303·04 (5)	13689·1	γ (3, 3) R_b	+ 1·3	+ 1·7
7589·62 (8)	13172·3	γ (0, 1) R_a	+ 0·5	+ 0·5
7596·03 (3)	13161·1	γ (0, 1) Q_a		
7628·13 (8)	13105·8	γ (0, 1) R_b	+ 0·2	+ 0·7
7634·08 (4)	13095·6	γ (0, 1) Q_b		
7666·43 (6)	13040·3	γ (1, 2) R_a	+ 0·6	− 0·1
7672·10 (10)	13030·7	γ (0, 1) R_c γ (1, 2) Q_a	+ 0·5	+ 0·2
7679·33 (4)	13018·4	γ (0, 1) Q_c		
7705·21 (8)	12974·7	γ (1, 2) R_b	+ 0·4	+ 1·0
7713·40 (4)	12960·9	γ (1, 2) Q_b		
7743·24 (4)	12910·9	γ (2, 3) R_a	+ 0·4	+ 0·1
7749·76 (4)	12900·1	γ (1, 2) R_c γ (2, 3) Q_a	+ 0·9	+ 1·0
7755·82 (4)	12890·0	γ (1, 2) Q_c		
7783·44 (2)	12844·3	γ (2, 3) R_b	− 0·1	+ 0·2
7820·11 (8)	12784·0	γ (3, 4) R_a	− 0·2	+ 0·9
7828·04 (10)	12771·1	γ (2, 3) R_c γ (3, 4) Q_a	+ 1·5	+ 1·6
7861·00 (6)	12717·5	γ (3, 4) R_b	+ 1·5	+ 1·1
7900·92 (4)	12653·3	γ (4, 5) R_a (?)	− 7·5	− 4·0
7907·33 (6)	12643·0	γ (3, 4) R_c γ (4, 5) Q_a	+ 1·8	+ 1·2
7948·60 (8)	12577·4	γ (4, 5) Q_b		
7988·05 (4)	12515·3	γ (4, 5) R_c	+ 1·1	− 0·7
7995·98 (2)	12502·8	γ (4, 5) Q_c		

There is no conclusive evidence for a term in $(n' + \frac{1}{2})(n'' + \frac{1}{2})$, the coefficient of which is usually small, and may here be indeterminable on account of uncertainty in the exact position of the heads; the absence of this term would indicate that the R head is near the origin. Table 4 is too incomplete and the data insufficiently accurate for the determination of vibrational constants from the Q heads; these limitations are due to the facts that these fainter heads become lost in the overlapping sequences, and that the heads are not sufficiently well defined for accurate measurement.

Table 2. R and Q heads of the orange system β

n''		0		1		2		3		4
n'										
0	R	17859·1								
	Q	17840·1								
	ΔR		99·8							
	ΔQ		99·7							
1	R			17759·3						
	Q			17740·4						
	ΔR				101·2					
	ΔQ				101·1					
2	R					17658·1				
	Q					17639·3				
	ΔR						101·9			
	ΔQ						102·2			
3	R							17556·2		
	Q							17537·1		
	ΔR								101·2	
	ΔQ								100·3	
4	R									17455·0
	Q									17436·8

§ 5. ANALYSIS OF STRUCTURE

The equations for the triplet sequences of the heads in Table 3, in the form obtained by means of the new quantum mechanics, are:

$$\left.\begin{aligned}
\nu &= 14243{\cdot}7 + \{864{\cdot}60\,(n' + \tfrac{1}{2}) - 3{\cdot}675\,(n' + \tfrac{1}{2})^2\} \\
&\qquad - \{1009{\cdot}85\,(n'' + \tfrac{1}{2}) - 5{\cdot}125\,(n'' + \tfrac{1}{2})^2\} & \ldots\ldots(a) \\
\nu &= 14175{\cdot}5 + \{866{\cdot}27\,(n' + \tfrac{1}{2}) - 3{\cdot}81\,(n' + \tfrac{1}{2})^2\} \\
&\qquad - \{1008{\cdot}15\,(n'' + \tfrac{1}{2}) - 4{\cdot}54\,(n'' + \tfrac{1}{2})^2\} & \ldots(2)\ldots.(b) \\
\nu &= 14100{\cdot}7 + \{867{\cdot}57\,(n' + \tfrac{1}{2}) - 3{\cdot}98\,(n' + \tfrac{1}{2})^2\} \\
&\qquad - \{1009{\cdot}15\,(n'' + \tfrac{1}{2}) - 4{\cdot}64\,(n'' + \tfrac{1}{2})^2\} & \ldots\ldots(c).
\end{aligned}\right\}$$

According to these equations the separations of the triplets, expressed in wave-numbers, depend on n, but Tables 3 and 4 seem to indicate accidental rather than real variations in them; this discrepancy may be due to the fact that the measurements were made on the heads. If the separations are constant, the coefficients of $(n + \frac{1}{2})$ and $(n + \frac{1}{2})^2$ would be the same for R_a, R_b and R_c, and then the wave-numbers of the heads would be given by equation (3):

$$\nu = \begin{Bmatrix} 14242{\cdot}6 \\ 14175{\cdot}9 \\ 14101{\cdot}3 \end{Bmatrix} + \{866{\cdot}24\,(n' + \tfrac{1}{2}) - 3{\cdot}82\,(n' + \tfrac{1}{2})^2\} - \{1009{\cdot}07\,(n'' + \tfrac{1}{2}) - 4{\cdot}75\,(n'' + \tfrac{1}{2})^2\} \quad \ldots\ldots(3),$$

where the coefficients are obtained from averages of Δa, Δb and Δc in a given triple row or column of Table 3. Since the evidence for constant separation is indecisive, wave-numbers have been calculated from equations (2) and (3), and the differences between these and those observed are shown in columns (4) and (5) of Table 3.

For the sake of comparison with Birge and Christy's equation* for the blue-green system α, their equation is converted from the form of the older quantum theory to the form used above and becomes:

$$\begin{matrix}(a)\\(b)\\(c)\end{matrix}\quad \nu = \begin{Bmatrix}19434{\cdot}48\\19432{\cdot}58\\19423{\cdot}75\end{Bmatrix} + \{837{\cdot}86\,(n' + \tfrac{1}{2}) - 4{\cdot}546\,(n' + \tfrac{1}{2})^2\} - \{1008{\cdot}12\,(n'' + \tfrac{1}{2}) - 4{\cdot}519\,(n'' + \tfrac{1}{2})^2\}.$$

It is obvious that since the coefficients of $(n'' + \frac{1}{2})$ and $(n'' + \frac{1}{2})^2$ are the same in equation (2) as in Birge and Christy's equation, the final energy level in system γ, exhibited in Table 3, is the same as that of system α, analysed by those authors. In the latter the evidence obtained by them for the character of the electronic transition is most in favour of $^3\Pi \rightarrow {}^3\Pi$. They regarded the final state as the lowest excited $^3\Pi$ state of the TiO molecule, and by analogy with CO they suggested that the normal state is of the $^1\Sigma$ type.

It was suggested to the author by Mr R. W. B. Pearse that the molecule TiO with thirty electrons might resemble in electronic configuration the atom Ca with ten fewer electrons, and that the character of the electronic transitions responsible for the new systems β and γ might be found by comparison with the transitions responsible for the more prominent singlets and triplets of Ca.

The resemblance in electronic configuration between a molecule and an atom of ten fewer electrons implies, according to Pearse, that each constituent of the molecule not only retains its own two K electrons but also has a complete ring of eight L electrons. If this is true, then for the molecule TiO, O, having gained two electrons from Ti, resembles as a constituent of the molecule inactive Ne, while Ti having lost two electrons resembles Ca; herein lies a feasible explanation of the resemblance in transitions of Ca and TiO.

In Ca the normal ("ground") state is $4\,^1S$ and the lowest four excited states are $4\,^3P$, $4\,^1P$, $4\,^3S$ and $5\,^3P$ as shown in Fig. 1 (*a*), the well-known flame line λ 4226·73, ν 23652·4 being due to $4\,^1P \rightarrow 4\,^1S$† and the orange triplet $\lambda\lambda$ 6102·72, 6122·22, 6162·18, $\nu\nu$ 16381·7, 16329·5, 16223·6 to the transition $4\,^3S \rightarrow 4\,^3P$. The transition $5\,^3P \rightarrow 4\,^3P$ is, of course, not represented in the atomic spectrum by an observed triplet, but the wave-number corresponding to it may be obtained from the known values of the Ca terms; since the ratio of wave-numbers of the various analogous electronic transitions in atoms and molecules is only roughly the same, and since the transitions involve such numbers as 20000, it is immaterial which members of the ^3P terms are used. Thus, taking the middle terms, we obtain:

$$5\,^3P_1 \rightarrow 4\,^3P_1 = 34094{\cdot}6 - 12750{\cdot}2 = 21344{\cdot}4.$$

Comparing this number with ν_e obtained by Birge and Christy, we get for the Ca/TiO ratio:

$$\frac{21344{\cdot}4}{19432{\cdot}6} = 1{\cdot}1.$$

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[*] By private communication, also *Phys. Rev.* **33**, 701 (1929).

[†] Fowler, *Report*, p. 122–4.

Table 3. *R* heads of bands in red-infra-red system γ

n''		0		$\Delta''a$ $\Delta''b$ $\Delta''c$	1		$\Delta''a$ $\Delta''b$ $\Delta''c$	2		$\Delta''a$ $\Delta''b$ $\Delta''c$	3		$\Delta''a$ $\Delta''b$ $\Delta''c$	4		5
n'	*a*	14171·4	66·7	999·1	13172·3	66·5										
0	*b*	14104·7	74·6	998·9	13105·8	75·2										
	c	14030·1		999·5	13030·6											
	$\Delta'a$	858·7			857·8											
	$\Delta'b$	858·9			858·7											
	$\Delta'c$	859·3			858·2											
	a	15030·1	66·5	1000·0	14030·1	65·6	989·8	13040·3	65·6							
1	*b*	14963·6	74·2	999·1	13964·5	74·7	989·8	12974·7	74·6							
	c	14889·4		999·6	13889·8		989·7	12900·1								
	$\Delta'a$	....			848·5			849·3								
	$\Delta'b$	851·1			851·1			850·4								
	$\Delta'c$	853·5			851·5			852·5								
	a	......			14878·6	63·0	989·0	13889·6	64·5	978·7	12910·9	66·6				
2	*b*	15814·7	71·8	999·1	14815·6	74·3	990·5	13825·1	72·5	980·8	12844·3	73·2				
	c	15742·9		1001·6	14741·3		988·7	13752·6		981·5	12771·1					
	$\Delta'a$				....			843·0			841·7					
	$\Delta'b$				843·3			844·0			844·8					
	$\Delta'c$				845·0			841·4			....					
	a				......		....	14732·6	63·5	980·0	13752·6	63·5	968·6	12784·0	66·5	
3	*b*				15658·9	72·6	989·8	14669·1	75·1	980·0	13689·1		971·6	12717·5	74·5	
	c				15586·3		992·3	14594·0		....	......		....	12643·0		
	$\Delta'a$							....			835·4					
	$\Delta'b$							836·0			833·7					
	$\Delta'c$							836·2			....					
	a							......		....	14588·0	65·2		......		12653·3
4	*b*							15505·4	75·2	982·6	14522·8	74·9		......		......
	c							15430·2		982·3	14447·9			......		12515·3
	$\Delta'a$							....			....					
	$\Delta'b$							....			827·8					
	$\Delta'c$							828·6			828·7					
	a							......			......		....	14447·9		
5	*b*							......			15350·6	74·0	....	......		
	c							16258·9		982·3	15276·6		971·3	14305·3		
7	*a*										17051·3					

Table 4. *Q* heads of bands in red-infra-red system γ

n'			0		$\Delta''a$ $\Delta''b$ $\Delta''c$	1		$\Delta''a$ $\Delta''b$ $\Delta''c$	2		$\Delta''a$ $\Delta''b$ $\Delta''c$	3	$\Delta''a$ $\Delta''b$ $\Delta''c$	4	5	
n'	*a*		14160·4	66·4	999·3	13161·1	65·5									
0	*b*		14094·0	75·3	998·4	13095·6	77·2									
	c		14018·7		1000·3	13018·4										
		$\Delta'a$	855·6			857·6										
		$\Delta'b$	858·7			858·6										
		$\Delta'c$	861·0			859·7										
	a		15016·0	63·3	997·3	14018·7	64·5	988·1	13030·6	69·7						
1	*b*		14952·7	74·1	998·5	13954·2	76·1	993·3	12960·9	70·9						
	c		14878·6		1000·5	13878·1		988·1	12890·0							
		$\Delta'a$	....			849·5			847·6							
		$\Delta'b$	....			852·6			....							
		$\Delta'c$	854·0			854·5			853·9							
	a		......			14868·2	61·4	990·0	13878·2		978·1	12900·1				
2	*b*		......			14806·8	74·2	....	......		....	......				
	c		15732·6		1000·0	14732·6		988·7	13743·9		....	......				
		$\Delta'a$							....			843·8				
		$\Delta'b$							....			....				
		$\Delta'c$							844·0			....				
	a								......		....	13743·9	972·8	12771·1		
3	*b*								14658·5	70·5	....	......	....	......		
	c								14588·0		....	......	....	......		
		$\Delta'a$							....			833·6				
		$\Delta'b$							....			....				
		$\Delta'c$							831·2			....				
	a					......			......		....	14577·5		......	12643·0	65·6
4	*b*					16484·3			......		....	......		......	12577·4	74·6
	c					......			15419·2		....	......		......	12502·8	
		$\Delta'a$										....		....		
		$\Delta'b$										....		....		
		$\Delta'c$										....		....		
	a											......		14435·0		
5	*b*											15339·6		......		
	c											......		......		
												....				
												....				
												....				
	a											......				
6	*b*											......				
	c											16085·0				

Now for the infra-red system γ, Equation (2), the ν_e values of the origin are about 14233, 14165, 14090, and the Ca lines comparable with these will be expected to lie in the neighbourhood of $\nu\nu$ 15656, 15582, 15499 (obtained by multiplying the TiO values by 1·1); these are not far from the orange Ca triplet $4\,^3S \rightarrow 4\,^3P$, mentioned above.

Again for the orange system β the (0, 0) band head is at ν 17859 and ν_e is not far removed therefrom, say $\nu_e \div 17840 + 100/2 = 17890$; the corresponding Ca line would be expected in the neighbourhood of $17890 \times 1{\cdot}1 = 19679$. The nearest strong Ca line to this is the flame line $4\,^1P \rightarrow 4\,^1S$, ν 23652·4.

We may then tentatively assign to system γ a transition $^3\Sigma \rightarrow {}^3\Pi$, the final $^3\Pi$ state being also that of the blue-green system α; likewise we may assign to system β a transition $^1\Pi \rightarrow {}^1\Sigma$, the final $^1\Sigma$ state being the normal state of the TiO molecule, as was conjectured by Birge and Christy. These interpretations are in accordance with the facts (1) that both the systems β and γ have strong Q branches, as we should expect from a transition $\Pi \rightleftarrows \Sigma$, and (2) that each band of system γ has three R and three Q heads, while each band of system β has only one R and one Q head.

Accepting these electronic transitions for systems β and γ, we are still unable to construct an energy level diagram for TiO, for lack of a system which could be attributed to a transition between one of the triplet states and one of the singlet states. In order to make a possible representation of the TiO energy levels, we must further invoke the Ca/TiO ratios used above. Now in Ca the difference $4\,^1S - 4\,^3P$ works out to be $\nu\nu$ 15316, 15210, 15158. We may for the present take ten-elevenths of these values to represent the corresponding differences $^3\Pi - {}^1\Sigma$ in TiO, and thus roughly locate the lowest excited state $^3\Pi$ with respect to the normal state $^1\Sigma$. This is the basis on which Fig. 1 (*b*) has been constructed. With one exception the triplet separations in both Figs. 1 (*a*) and 1 (*b*) have been magnified about ten times; that exception is in the case of the vertical lines representing the triplet in the α system of TiO, the separations between which have been magnified about a hundred times.

Finally we may conclude that the $\Delta\nu$ separation of the triplets, namely, $Q_a - Q_b = 66$ and $Q_b - Q_c = 75$ cm.$^{-1}$, found for system γ, pertains to the $^3\Pi$ level and therefore also to the final level of the blue-green system α. Combining these final $^3\Pi$ separations with Birge and Christy's $\Delta\nu_R$ differences for system α, namely, $R_a - R_b = 1{\cdot}9$, $R_b - R_c = 8{\cdot}8$, we find for the initial $^3\Pi$ state the approximate separations $\Delta\,^3\Pi = 64$ and 66 cm.$^{-1}$.

§ 6. ACKNOWLEDGMENTS

The author thanks most appreciatively Prof. A. Fowler for his valuable suggestions, guidance and criticisms during the execution of this work; also Dr W. Jevons and Mr R. W. B. Pearse for their kind criticisms and help in the analysis of the gross structure of the bands of system γ.

§ 7. DESCRIPTION OF PLATE

Spectrograms of TiO *bands from* λ 5600–λ 8800.

(*a*) From panchromatic plate, exposure 22 seconds, showing the 0 sequence of the orange system β and some bands not treated in this paper.

(*b*) From panchromatic plate, exposure 22 seconds, showing (2, 0) band of system γ and some bands not treated in this paper.

(*c*) From panchromatic plate, exposure 30 seconds, showing three bands of the −2 sequence, three of the −1 sequence, and a few not treated in this paper.

(*d*) and (*e*) From kryptocyanine plates, exposure 16 and 9 minutes respectively; both show the −1, 0 and part of the +1 sequences of system γ.

(*f*) From neocyanine plate, exposure 90 minutes, showing the 0 and +1 sequences of system γ.

The wave-length scale is only approximate.

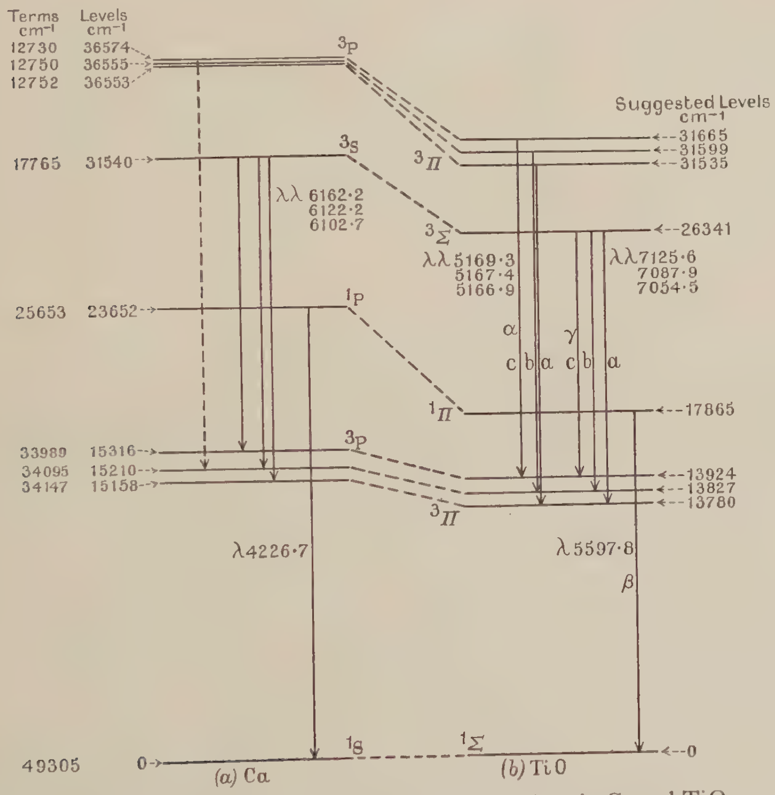

Fig. 1. Comparison of electronic energy transitions in Ca and TiO.

DISCUSSION

Dr W. Jevons: I congratulate the author on showing the connection between the two new systems β and γ and the previously known system α, on the "rotational" analysis of which she had already spent much time and thought when Birge and Christy's successful result was first announced. It should be pointed out that Miss Lowater announced the discovery and interpretations of both systems β and γ in *Nature*, April 27, and that since the completion of her present paper Christy has arrived at a similar result for γ only (*Nature*, June 8).

In 1924 I analysed the $^1\Pi \rightarrow {}^1\Sigma$ system of SiO, corresponding to the "4th positive" system of CO; it now appears that the analogous system of TiO (the monoxide of the next atom of column 4 of the periodic table) is Miss Lowater's system β, and it is interesting to note that although in CO and in SiO this transition is represented by a rather extensive system in the ultraviolet, in TiO it gives only a one-sequence system in the orange region. As CO gives about nine known systems and TiO three, one would expect SiO to have more than one system already analysed and the few unassigned bands recorded by Cameron*, and it would be well if Miss Lowater could include in her work on these oxides an examination of SiO in the red and infra-red regions.

The occurrence in the galley proof, § 2, of the notation TiI for the spectrum of the neutral atom Ti, reminds me that many workers share my own opinion that this notation MI, MII, MIII, ..., first used by the late Sir Norman Lockyer, for what we now know to be the spectra of the atom and its ions, should be abandoned in favour of the more definite and informative notation M, M^+, M^{++}, ... As usually printed MI looks more like an iodide than an atom. I personally have to pause a little to recall the fact that the degree of ionisation is one less than the affixed Roman numeral.

Mr C. V. Jackson: I thoroughly agree with Dr Jevons' suggestion, but I regard the new notation as a sad consequence of the sometimes excessive lack of conservatism of spectroscopists. For cases such as Millikan's "stripped atoms," e.g. SVI, it is perhaps easier to put the Roman numeral notation than to write S^{+++++}. But for cases of singly or doubly ionised atoms the M^+ notation is more expressive and eliminates the irritating mental arithmetic needed for the other notation. But perhaps the case is somewhat similar to that of the notation used for spectral terms. Before terms of higher multiplicity, then triplet, were discovered the beautiful notation of Fowler, viz. Capital, Greek and Italic letters for singlet, doublet and triplet terms respectively, was perfect, but when the higher multiplicities were found it was necessary to use the new notation, and for the sake of uniformity the singlet, doublet and triplet terms had to be expressed in it too. But the justification for the change from the M^+ notation for ionised atoms is not nearly so great as that for the change in the spectral term notation. However, it is gratifying to note that the M^+ notation has been used in the revision of Rowland's *Solar Wavelength Tables* (1928). The "stripped atom" of Cl, for instance, would, I submit, be denoted better by Cl^{6+} than by the usual ClVII.

Dr W. Jevons: The difficulty mentioned by Mr Jackson can be met by the use of index numerals.

Author's reply: I thank Dr Jevons for his criticism and kind remarks. With regard to the symbol TiI, I took it direct from Russell's paper in the *Astrophysical Journal*, regarding this as authoritative.

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* *Phil. Mag.* **3**, 110 (1925).

NOTES ON SOME RADIATION HEAT TRANSFER FORMULAE

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ABSTRACT. The general expression for the radiation heat transfer from a surface is irst considered, after which some simple cases are examined, i.e., parallel planes, concentric spheres, etc. Some general conclusions are then drawn for the case of a surface completely surrounded by other surfaces at a uniform temperature, but of no particular simple shape; it is pointed out that whatever the shapes, sizes, and relative positions of the various surfaces, the heat transfer per unit area must always lie between minimum and maximum values depending only upon temperatures and emissivities.

Lastly, an approximate formula is given for the heat transfer when the surroundings are poor reflectors; this is applied to two non-concentric spheres, one within the other.

§ 1. INTRODUCTION

The following notes contain some simple results dealing principally with the effects of reflected radiation upon the transfer of heat between a surface and its surroundings. The ground covered is to some extent semi-familiar, partly through the medium of analogous problems in optics, but so far as the author is aware the majority of the conclusions have not previously been pointed out.

§ 2. GENERAL FORMULA

The net rate of heat transfer by radiation from a surface at a known temperature T° C. absolute in the presence of other surfaces at any maintained temperatures, is given by

$$H = \sigma e (1 - K)(T^4 - T_0^4) \text{ cals. per sq. cm. per sec.} \qquad \ldots\ldots(1),$$

where e is the emissivity of the surface (assumed grey);
σ Stefan's constant ($1{\cdot}36 \times 10^{-12}$ C.G.S. units);
K the fraction of the radiation, emitted from the surface in question, which is returned to it by reflection from other surfaces and reabsorbed;
T_0 the equilibrium temperature (absolute) which the surface would tend to attain under the influence of radiation alone, if no heat were supplied to or withdrawn from it.

This result is easily proved. From the above definition of K it follows that the heat loss from the surface per unit area per second, taking into account only its own emission, is equal to $\sigma e (1 - K) T^4$. Since K is independent of the surface temperature T, the corresponding heat loss at the equilibrium temperature T_0 would be $\sigma e (1 - K) T_0^4$.

The heat gained by the given surface per unit area per second, owing to absorption of radiation emitted from other surfaces, does not depend upon the temperature of the given surface, and must therefore be equal to $\sigma e (1 - K) T_0^4$ since in equilibrium the surface gains as much heat as it loses. Hence the expression for the heat loss from the surface when it is maintained at temperature T is given by the difference between $\sigma e (1 - K) T^4$ and $\sigma e (1 - K) T_0^4$, i.e. by equation (1). The values of K and T_0 depend in general upon the sizes, shapes, and relative positions of the various surfaces, as well as upon their temperatures and emissivities.

§ 3. SURFACE COMPLETELY SURROUNDED BY OTHER SURFACES AT A UNIFORM TEMPERATURE

In this case the equilibrium temperature T_0 is, from the properties of a uniform temperature enclosure, equal to the uniform temperature T' of the surrounding surfaces. There remains the evaluation of K, which takes account of reflected radiation, and may be of considerable importance in some cases. It will be more convenient to consider one or two simple shapes of surfaces before coming to some general conclusions as to the limits within which K may vary.

§ 4. PARALLEL PLANE SURFACES

The radiation emitted from either surface undergoes reflection at each of the two surfaces alternately, and it is easily proved that

$K = e(1 - e')/(e + e' - ee')$ where e, e' are the emissivities of the two surfaces.

Equation (1) for the heat transfer per unit area per second from either surface therefore becomes

$$H = \frac{\sigma ee'}{e + e' - ee'} (T^4 - T'^4) \qquad \text{......(2).}$$

This particular result is well known, and is to be found in standard books on heat.

§ 5. CONCENTRIC SPHERES OR CYLINDERS

(*a*) *Internal surface of outer sphere (or cylinder) regularly reflecting.* From a brief consideration of the paths of the rays in these particular geometrical arrangements it will be seen that all the radiation emitted from the inner surface must, after suffering regular reflection at the outer surface, fall directly upon the inner surface again; this is true both for concentric spheres and concentric cylinders.

It makes no difference whether the inner sphere (or cylinder) is a regular or diffuse reflector; in either case the radiation reflected from it is incident upon it again after reflection at the outer surface, and so on. The radiation from the inner surface is therefore reflected at the outer and inner surfaces alternately, and the value of K is precisely the same as in the case of parallel plates already considered. The formula for the heat transfer is therefore the same as (2).

(*b*) *Internal surface of outer sphere* (*or cylinder*) *diffusely reflecting*. The radiation rom the inner surface, after diffuse reflection at the outer surface, does not all fall again directly upon the inner surface, but some of it strikes other parts of the outer surface. Suppose ρ to represent the fraction of the diffusely reflected radiation which strikes the inner surface directly: the fraction $(1-\rho)$ undergoes another diffuse reflection at the outer surface, after which a fraction ρ of it is incident directly upon the inner surface, and so on. The total fraction of the emission from the inner surface which is again incident upon that surface after the series of outer-surface reflections is by addition equal to

$$\rho(1-e') + \rho(1-\rho)(1-e')^2 + \dots = \rho(1-e')/(\rho + e' - \rho e') = q, \text{ say.}$$

Part of the radiation thus returned to the inner surface is reflected from it and undergoes a series of outer-surface reflections similar to those just described in the case of the original emission.

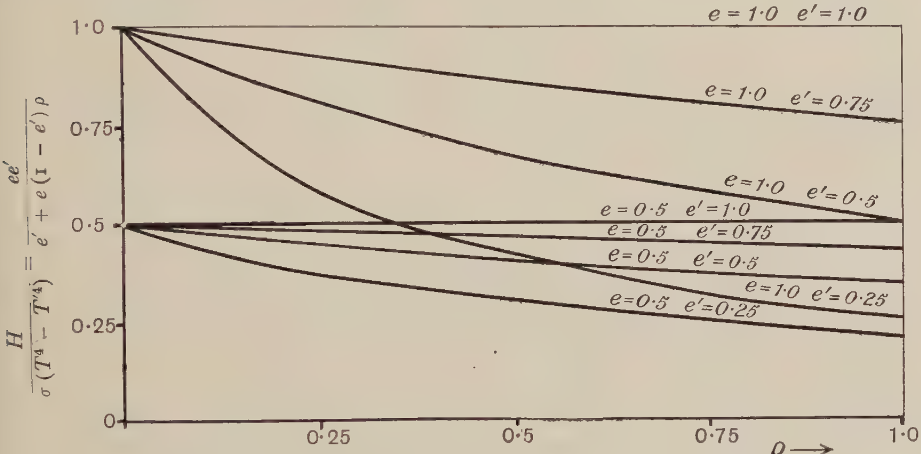

Fig. 1. Radiation between concentric cylinders or spheres.

Finally, these reflections are repeated indefinitely, and the fraction of the inner surface emission ultimately returning to it and undergoing reabsorption is given by

$$K = eq + eq^2(1-e') + \dots = e\rho(1-e')/(e' + \rho e - \rho e e').$$

The expression for the net radiation heat transfer is therefore, from (1),

$$H = \frac{\sigma e e'}{e' + e(1-e')\rho}(T^4 - T'^4) \qquad \dots\dots(3).$$

This result is shown graphically in Fig. 1.

The value of ρ may be expressed in terms of the radii a, b, of the inner and outer spheres (or cylinders) respectively. It is easily shown, from the usual cosine distribution law for diffuse reflection, that for concentric cylinders $\rho = a/b$, and for concentric spheres $\rho = a^2/b^2$. In either case ρ is equal to the ratio of corresponding areas of the inner and outer surfaces.

It will be noted that, as would be expected, expression (3) becomes identical with (2) as $\rho \to 1$.

Since completing the present notes the author has found that the result (3) is given by M. ten Bosch in his recent book *Die Wärmeübertragung*. The method of proof employed by M. ten Bosch is, however, considerably lengthier than the above, and no distinction is drawn between the cases of regular and diffuse reflectors.

§ 6. SOME GENERAL CONCLUSIONS FOR THE CASE OF A SURFACE COMPLETELY SURROUNDED BY OTHERS AT A UNIFORM TEMPERATURE

It is important to determine generally the conditions under which the influence of reflected radiation (i.e. K) may be of practical importance.

In the first place it will be noted that if $e' = 1{\cdot}0$, i.e. if the surrounding surfaces are perfect absorbers, $K = 0$ whatever the shapes, sizes and relative positions of the surfaces, and (1) becomes

$$H = \sigma e\,(T^4 - T'^4),$$

which is the usual simple formula employed in heat transfer calculations. This result is therefore strictly valid for "black" surroundings, from which of course no radiation is reflected.

If the surrounding surfaces are not perfect absorbers, the heat loss from the inner surface is less, to an extent depending upon K, equation (1), than it would be if they were black; obviously, the better the reflecting power of the surroundings (i.e. the smaller e'), the greater K and the smaller the heat loss, other things being equal. But for surfaces of given emissivities K depends upon the shapes, sizes and relative positions of the inner and outer surfaces. Generally speaking the influence of reflected radiation is least (K least) when the inner surface has linear dimensions small in comparison with its surroundings, and is greatest when the inner and outer surfaces are of the same order of size, the conditions in the latter case closely approximating to those which hold in the case of parallel plates.

The influence of changes in the emissivity of the surrounding surfaces upon the heat transfer is least when the inner surface is relatively small; e' does not appear in the simple expression $H = \sigma e\,(T^4 - T'^4)$. It is greatest when the two surfaces are nearly the same size, for e and e' appear symmetrically in equation (2).

The case of two concentric cylinders or spheres, the outer one having a regularly reflecting internal surface, is exceptional in that the relative sizes make no difference to the heat transfer, but it may be pointed out that if the inner sphere or cylinder were small and slightly eccentrically placed, the heat loss would be considerably greater than when it is in the concentric position, since the geometrical conditions for the return of reflected radiation to the inner surface would no longer be fulfilled.

To sum up, it is interesting to note that, for given inner and outer surface emissivities e and e' respectively, the heat transfer must always lie between a maximum value given by $H = \sigma e\,(T^4 - T'^4)$ and a minimum value given by

$H = \sigma ee' (T^4 - T'^4)/(e + e' - ee')$ whatever the shapes, sizes, relative positions, etc. of the surfaces. These two values may conveniently be read off from Fig. 1 in which they are represented by the ordinates corresponding to $\rho = 0$ and $\rho = 1$ respectively.

The maximum value corresponds to perfectly absorbing surroundings, and the minimum value to plane parallel surfaces. It will be seen from Fig. 1 that if the surroundings are not particularly good reflectors (e' not far from unity), these two expressions do not differ greatly. For instance, if e and e' are both equal to 0·50, H must lie between 0·50 and 0·33 times $\sigma (T^4 - T'^4)$; and if $e = e' = 0{\cdot}75$, H lies between 0·75 and 0·60 times $\sigma (T^4 - T'^4)$.

With many ordinary surroundings e' would be about 0·90, and since in this case H cannot differ from the maximum value $\sigma e (T^4 - T'^4)$ by more than 10 per cent. under any conditions, whatever the value of e, this simple formula cannot lead to very great error under such circumstances.

Nevertheless in some cases, as, for instance, with a calorimeter closely surrounded by an enveloping box, the reflected radiation may be by no means negligible. It is clear from the above considerations that, whereas coating the surface of a relatively small hot body with aluminium paint reduces the radiation heat transfer from the body to its surroundings in direct proportion to the change of surface emissivity, a similar treatment of the walls of the room in which the body is situated has no effect upon the heat loss.

On the other hand if the body were comparable in size with the room surrounding it, the heat loss, for given surface temperatures, would be reduced to practically the same extent by the coating of either the body or the surrounding walls with aluminium paint, assuming of course that both surfaces have the same emissivity before painting.

In the particular case of an ordinary vacuum flask with two silvered (regularly reflecting) concentric cylindrical surfaces, the conditions are the same as for parallel plates, as has been shown in § 5 (*a*), and the silver coatings on the inner and outer surfaces are equally effective in diminishing radiation heat loss.

§ 7. APPROXIMATE EXPRESSION FOR *K* WHEN THE DIFFUSE REFLECTING POWER OF THE SURROUNDING SURFACES IS SMALL. CASE OF TWO NON-CONCENTRIC SPHERES

If the surrounding surfaces are poor enough reflectors for radiation undergoing more than one reflection at them to be neglected, K may be expressed in terms of integrals taken over the inner and outer surfaces.

If dS, dS' denote elementary areas of the inner and outer surfaces respectively, and θ, θ' represent the angles made by the normals to these areas with the line of length r joining them, the amount of radiation falling every second upon dS' from those parts of the inner surface which are visible from dS' is given by

$$EdS' \int \frac{\cos\theta . \cos\theta' dS}{\pi r^2} = \phi EdS', \text{ say} \qquad \ldots\ldots(4),$$

where E represents the radiation emitted from the inner surface in all directions per unit area per second and the integral extends over the part of the inner surface facing dS'.

The part of this radiation which, after diffuse reflection at dS', falls upon the inner surface is given by

$$(1 - e')\,\phi E dS' \int \frac{\cos\theta \, . \cos\theta' dS}{\pi r^2},$$

where the integral is to be taken over the part of the inner surface facing dS', and is therefore identical with ϕ as defined in (4). Hence the radiation from the parts of the inner surface facing dS' which returns to the inner surface after reflection at dS' is given by

$$(1 - e')\,\phi^2 E dS'.$$

Finally, integrating for all elements of area of the outer surface, we find that the radiation from the whole of the inner surface which returns to it per second after reflection at the outer surface is equal to

$$E(1 - e') \int \phi^2 dS'.$$

Since the inner surface absorbs a fraction e of the radiation falling upon it, and the total emission from the whole of the inner surface is ES,

$$K = \frac{e(1 - e')}{S} \int \phi^2 dS' \qquad \text{......(5)},$$

where S denotes the total inner surface area, and the integral extends over the entire outer surface. No other reflected radiation need be taken into account since it has been postulated that radiation which has undergone more than one reflection at the outer surface is of negligible intensity.

As an example, consider the particular case of two non-concentric spheres one within the other. The value of ϕ at any point on the outer sphere at a distance x from the centre of the inner sphere is easily seen from (4) to be equal to

$$a^2 (b^2 + x^2 - c^2)/2\pi b x^3,$$

where a and b are the radii of the inner and outer spheres and c is the distance apart of their centres ($c < b - a$).

Hence from (5) the value of K is given by

$$\begin{aligned} K &= \frac{e(1 - e')\,a^2}{8bc} \int_{b-c}^{b+c} \frac{(b^2 + x^2 - c^2)^2\,dx}{x^5} \\ &= \frac{e(1 - e')\,a^2}{8b} \left\{ \frac{2b(3b^2 - c^2)}{(b^2 - c^2)^2} + \frac{1}{c} \log_e \frac{b + c}{b - c} \right\} \qquad \text{......(6)}. \end{aligned}$$

It will be noted from (6) that as c varies between $+(b - a)$ and $-(b - a)$, K has a minimum value equal to $e(1 - e')\,a^2/b^2$ when $c = 0$, and increases the further the inner sphere is moved from the concentric position.

Hence from (1) the heat transfer for spheres of given sizes, emissivities and temperatures, is greatest in the concentric position. It must be remembered of course that this has only been proved for the case where the outer sphere has a poor enough internal surface reflecting power for radiation suffering more than one reflection at it to be neglected.

If $b = 2a$, $e = e' = 0{\cdot}75$, it is found from (1) and (6) that when

$$c = 0, \quad H = {\cdot}715\,\sigma\,(T^4 - T'^4),$$

and when

$$c = a, \quad H = {\cdot}697\,\sigma\,(T^4 - T'^4),$$

the latter case corresponding to the geometrical arrangement in which the spheres touch one another. The difference between the two cases is therefore very small from a practical point of view.

A METHOD OF EVALUATING THE KINEMATIC COEFFICIENTS OF LINKED SYSTEMS

By T. SMITH, M.A., F.Inst.P.

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ABSTRACT. The coefficients in a function representing the energy of a system, or any function having analogous properties, may be combined to form a matrix such that the matrix of the combination of any number of systems is the product of the matrices of its parts.

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§ 1. THE PHYSICAL PROBLEM

The solution of many problems in mechanics, electrodynamics, and other branches of applied physics, is greatly facilitated by the construction of a function which represents in magnitude the kinetic energy of the system concerned, or alternatively the rate at which energy is being dissipated in the system. If the system itself contains no source of energy, any access of energy represents energy lost by the external stores from which the system can draw. This correspondence may be expressed in an equation from which the entire motion of the system can be derived. The necessary condition for the application of this method is that the energy function should be known. Its construction for some elementary systems is not difficult, and the choice of variables is to some extent arbitrary. Let us suppose these are chosen to relate to the channels by which energy can be supplied to the system; for example, in an electric network the variables may define the currents travelling along the connections with the external energy supplies. Now we may build up a more complex system by using some of these connections to couple the first system to another, of which the energy function is known, leaving the remaining channels of both systems as paths along which energy may reach the compound system. Since any gain of energy by the first system through couplings with the second system involves an equal loss of energy by the latter, the energy function of the compound system is the sum of those of the two separate parts. Before we can use this sum it must be expressed as a function of those variables alone which correspond to the external connections of the compound instrument. The conditions by means of which the variables common to the two parts must be eliminated will be seen at once if we realise that the exchanges of energy between the two parts will have the minimum values consistent with the existing flow from the external sources. Mathematically this means that the superfluous variables will be eliminated by imposing the condition that the sum of the two functions is independent of small variations in any or all of these variables.

The energy function will in general be an algebraic polynomial in several variables, and the properties of the system depend only on the values of the coefficients in this polynomial. When the solution of the dynamical equations has been obtained for a polynomial of a definite type, all particular problems for systems having energy functions of this class are solved by evaluating the coefficients alone. Very often the converse problem is of greater importance—to discover how to construct a system having given coefficients or given values for certain functions of the coefficients. The purpose of this paper is to show that the coefficients for complex systems, built by linking simpler systems together into a chain in the way described for two systems, may be found by matrix multiplication. For practical computation this form of solution has many advantages over those described in theoretical treatises—for example, treatises on electrodynamics. No more convenient form for dealing with the converse problem could be desired.

A characteristic property of the functions which greatly simplifies the problem is that the energy is expressible either exactly or with very good approximation by a quadratic function of the variables. We will assume in the first place that only second order terms exist, and discuss the more general case afterwards. The coefficients are not necessarily numerical constants: in many electrical problems they involve operators, and the following treatment is arranged to apply when the coefficients are of this kind.

§ 2. THE MATHEMATICAL PROBLEM

The essential mathematical problem is as follows. Let α, β, γ, δ ... ζ, η each denote a set of variables and $\mathscr{A}(\alpha, \beta)$, $\mathscr{B}(\beta, \gamma)$, $\mathscr{C}(\gamma, \delta)$ ... $\mathscr{X}(\zeta, \eta)$ symmetrical bilinear functions of the sets of variables indicated. When all the variables of sets β, γ, δ ... ζ are given the values which make the sum

$$\mathscr{A} + \mathscr{B} + \mathscr{C} + \ldots + \mathscr{X}$$

stationary, it may be expressed as a function of the variables of sets α and η alone. A method of finding the coefficients of this function is to be obtained.

Let us write α for the single row matrix of the first set of variables, arranged in a definite order, and α' for the conjugate matrix consisting of the same variables arranged in a single column. Similarly let $(\alpha\beta)$ be the single row matrix formed by set α followed by set β, and $\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix}$ its conjugate. We may then write without loss of generality

$$\mathscr{A} = (\alpha\beta)\, m_1 \begin{pmatrix}\alpha'\\ \beta'\end{pmatrix} \qquad \ldots\ldots 2\cdot 1,$$

where m_1 is a symmetrical square matrix of degree equal to the number of variables in sets α and β together, say n. The total number of elements in the matrix is n^2, of which n are in the principal diagonal. The remainder are equal in pairs, and the number of degrees of freedom in the matrix is thus

$$\tfrac{1}{2}(n^2 - n) + n = \tfrac{1}{2}(n^2 + n) \qquad \ldots\ldots 2\cdot 11.$$

Any matrix which is to represent this system must have the same number of degrees of freedom.

We may replace m_1 by

$$\begin{pmatrix} u_1 & w_1' \\ w_1 & v_1 \end{pmatrix} \qquad \ldots\ldots 2{\cdot}12,$$

where u_1 and v_1 are symmetric square matrices of degrees equal to the number of variables in systems α and β respectively, and w_1 is a general matrix, in general not square, and w_1' its conjugate. Equation 2.1 may now be written

$$\mathscr{A} = \alpha u_1 \alpha' + \alpha w_1' \beta' + \beta w_1 \alpha' + \beta v_1 \beta' \qquad \ldots\ldots 2{\cdot}13.$$

Considering now the combination of two systems, we have

$$\begin{aligned} \mathscr{A} + \mathscr{B} = \alpha u_1 \alpha' + \alpha w_1' \beta' + \beta w_1 \alpha' + \beta v_1 \beta' & \\ + \beta u_2 \beta' + \beta w_2' \gamma' + \gamma w_2 \beta' + \gamma v_2 \gamma' & \qquad \ldots\ldots 2{\cdot}2, \end{aligned}$$

and β and β' are to be eliminated in virtue of

$$\begin{aligned} \alpha w_1' x' + \beta v_1 x' + \beta u_2 x' + \gamma w_2 x' & \\ + x w_1 \alpha' + x v_1 \beta' + x u_2 \beta' + x w_2' \gamma' = 0 & \qquad \ldots\ldots 2{\cdot}21, \end{aligned}$$

where x is an arbitrary linear matrix having the same number of elements as there are variables in β, and x' is the conjugate of x. By putting β for x we see that the stationary value of $\mathscr{A} + \mathscr{B}$, which we will denote by $[\mathscr{A} + \mathscr{B}]$, is given by

$$\begin{aligned} [\mathscr{A} + \mathscr{B}] = \alpha u_1 \alpha' + \tfrac{1}{2}\, \alpha w_1' \beta' + \tfrac{1}{2}\, \beta w_1 \alpha' & \\ + \tfrac{1}{2}\, \beta w_2' \gamma' + \tfrac{1}{2}\, \gamma w_2 \beta' + \gamma v_2 \gamma' & \qquad \ldots\ldots 2{\cdot}22. \end{aligned}$$

The usual method of eliminating β and β' between 2·21 and 2·22 involves finding the conjugate reciprocal of $v_1 + u_2$, thence obtaining β and β' explicitly from 2·21, and substituting these values in 2·22. The process is evidently laborious, and it is an essential part of our aim to avoid it.

We first observe that the systems for which the matrices w are not square may be regarded as simplifications of systems in which they are square, the reduction in the variables being brought about by assuming the existence of linear relations between variables in the symmetrical case—very frequently pairs of variables are made equal to one another and are thenceforth represented by a single variable. As the method to be employed requires w to be square, we shall suppose that those simplifications are made after the calculation is completed or alternatively that w is augmented, in a manner consistent with the conditions of the problem, to render the matrix square. All the matrices represented by u, v, w are now square and of the same order, say n. The number of degrees of freedom of the system is obtained by writing $2n$ for n in 2·11, i.e. it is $2n^2 + n$.

§ 3. DEVELOPMENT OF A STABLE TYPE OF MATRIX

We require, then, to construct a square matrix of degree $2n$, of stable type, which has $2n^2 + n$ degrees of freedom. By stability is meant that the identities between the elements in the product of two such matrices shall correspond exactly to those of their factors. When this is the case the product of any number of matrices of this class will obviously itself be a member of the class, and it is unnecessary to consider more than two factors to establish the general laws.

Let p, q, r, s denote square matrices of degree n, in terms of which the following matrices of degree $2n$ are defined:

$$A = \begin{pmatrix} p_1 & s_1 \\ r_1 & q_1 \end{pmatrix}, \qquad A^* = \begin{pmatrix} q_1' & -s_1' \\ -r_1' & p_1' \end{pmatrix}$$

$$B = \begin{pmatrix} p_2 & s_2 \\ r_2 & q_2 \end{pmatrix}, \qquad B^* = \begin{pmatrix} q_2' & -s_2' \\ -r_2' & p_2' \end{pmatrix}$$

$$C = \begin{pmatrix} p_{12} & s_{12} \\ r_{12} & q_{12} \end{pmatrix}, \qquad C^* = \begin{pmatrix} q_{12}' & -s_{12}' \\ -r'_{12} & p_{12}' \end{pmatrix} \qquad \ldots\ldots 3\cdot 1,$$

where the accents as usual denote conjugate (or transposed) matrices.

Now let

$$AB = C \qquad \ldots\ldots 3\cdot 2,$$

so that

$$\begin{aligned} p_{12} &= p_1p_2 + s_1r_2, \\ q_{12} &= r_1s_2 + q_1q_2, \\ r_{12} &= r_1p_2 + q_1r_2, \\ s_{12} &= p_1s_2 + s_1q_2, \end{aligned}$$

and therefore

$$\begin{aligned} p_{12}' &= p_2'p_1' + r_2's_1', \\ q_{12}' &= s_2'r_1' + q_2'q_1', \\ r_{12}' &= p_2'r_1' + r_2'q_1', \\ s_{12}' &= s_2'p_1' + q_2's_1'. \end{aligned}$$

The last four equations are the conditions that

$$C^* = B^*A^* \qquad \ldots\ldots 3\cdot 21.$$

If then A and A^* are conjugate reciprocals, and similarly B and B^* are conjugate reciprocals, equations 3·2 and 3·21 show that C and C^* stand to one another in the same relation. In other words, the properties

$$AA^* = A^*A = 1 \qquad \ldots\ldots 3\cdot 3$$

are stable. The conditions implied by this relation may be expressed either as

$$\left.\begin{aligned} pq' - sr' &= 1 \\ -rs' + qp' &= 1 \\ ps' - sp' &= 0 \\ rq' - qr' &= 0 \end{aligned}\right\} \qquad \ldots\ldots 3\cdot 31,$$

or

$$\left.\begin{aligned} q'p - s'r &= 1 \\ -r's + p'q &= 1 \\ q's - s'q &= 0 \\ r'p - p'r &= 0 \end{aligned}\right\} \qquad \ldots\ldots 3\cdot 32.$$

If any one of the matrices p, q, r, s is non-singular—we shall assume it is r—the one set is easily derived from the other. The first two equations of each set are conjugate. The last equations of each set state that $r'p$ and qr' are symmetrical matrices. We may therefore write

$$p = ur, \qquad q = rv \qquad \ldots\ldots 3\cdot 4,$$

where u and v are each symmetrical, so that $p' = r'u$, $q' = vr'$. The first relation then gives

$$urvr' - sr' = 1,$$

or

$$urv - s = R' \qquad \ldots\ldots 3{\cdot}41,$$

where R' is the conjugate reciprocal of r'. The degrees of freedom of the system are therefore determined by those of r, u, v, i.e. the number is

$$n^2 + \tfrac{1}{2}(n^2 + n) + \tfrac{1}{2}(n^2 + n) = 2n^2 + n,$$

which is the number needed in the matrix we are seeking.

If we substitute for p, q and s from 3·3 and 3·31, we immediately find from the multiplication law

$$r_{12} = r_1 v_1 r_2 + r_1 u_2 r_2 \qquad \ldots\ldots 3{\cdot}5,$$

or

$$v_1 + u_2 = R_1 r_{12} R_2 \qquad \ldots\ldots 3{\cdot}51,$$

$$u_{12} = u_1 - R_1' r_2 R_{12} \qquad \ldots\ldots 3{\cdot}52,$$

$$v_{12} = v_2 - R_{12} r_1 R_2' \qquad \ldots\ldots 3{\cdot}53.$$

Since v_1 and u_2 are symmetric, 3·51 gives

$$R_1 r_{12} R_2 = R_2' r_{12}' R_1' \qquad \ldots\ldots 3{\cdot}6.$$

Multiplying before by $R_{12}' r_2'$ and behind by $r_2 R_{12}$ we obtain

$$R_{12}' r_2' R_1 = R_1' r_2 R_{12},$$

and thus by 3·52 u_{12} is symmetrical. Similarly v_{12} is symmetrical. The product of two matrices of the types represented by 3·1, 3·3 and 3·4 is thus in all essential respects similar to its factors.

§ 4. APPLICATION

In the second section we dealt with an expression involving two symmetrical matrices u and v, and a third matrix w. In the third section we have developed a matrix definable in terms of two symmetrical matrices u and v and a third matrix r. We will identify the u and v of the one section with those of the other, and consider whether we can usefully relate the remaining matrices.

By 3·41 we may replace 2·21 by

$$\alpha w_1' x' + \beta R_1 r_{12} R_2 x' + \gamma w_2 x' \\ + x w_1 \alpha' + x R_2' r_{12}' R_1' \beta' + x w_2' \gamma' = 0 \qquad \ldots\ldots 4{\cdot}1.$$

Comparison with 2·22 suggests that we assume

$$w = -R \qquad \ldots\ldots 4{\cdot}2.$$

Making this substitution and putting

$$x = \alpha R_{12}' r_2' + \gamma R_{12} r_1,$$

so that

$$x' = r_2 R_{12} \alpha' + r_1' R_{12}' \gamma',$$

as we are entitled to do since x is arbitrary and the quantities given are of the correct dimensions, we obtain

$$\begin{aligned}&2\,\alpha R_1{}'r_2R_{12}\alpha' - \alpha R_1{}'\beta' + 2\,\alpha R_{12}{}'\gamma' - \beta R_1\alpha' \\ &\quad - \beta R_2{}'\gamma' + 2\,\gamma R_{12}\alpha' - \gamma R_2\beta' + 2\,\gamma R_2r_1{}'R_{12}{}'\gamma' = 0 \qquad \ldots\ldots 4{\cdot}3.\end{aligned}$$

It at once follows from 2.22, 3.52 and 3.53 that

$$[\mathscr{A} + \mathscr{B}] = \alpha u_{12}\alpha' - \alpha R_{12}{}'\gamma' - \gamma R_{12}\alpha' + \gamma v_{12}\gamma' \qquad \ldots\ldots 4{\cdot}4,$$

which corresponds exactly to 2·13 from which we started. The properties of the compound system are therefore obtainable by simply multiplying together the matrices of the type discussed in the third section. The extension to a product containing any number of factors follows immediately.

§ 5. ALTERNATIVE EXPRESSIONS

It is well known that the properties of a system may be expressed in another way closely related to that which we have adopted. For example, the variables in the electrical problem may be the values of the potential at specified points instead of currents. In the mathematical development we observe that we could have developed expressions around the matrix s instead of around r. Equations 3·31 and 3·32 show that we may put

$$q = hs, \qquad p = sk \qquad \ldots\ldots 5{\cdot}1.$$

From 3·31 we also obtain

$$r = hsk - S' \qquad \ldots\ldots 5{\cdot}11,$$

corresponding to 3·41. Now let

$$\mathsf{A} + \mathscr{A} + a\alpha' + b\beta' + \alpha a' + \beta b' = 0 \qquad \ldots\ldots 5{\cdot}2$$

(this form being preferred on account of its formal symmetry), where A is a function of the variables in the linear matrices a and b alone. Thus variations in α and β make no difference to A, or from 2·13, on writing pR and Rq for u and v,

$$\begin{aligned}&ya' + yR'p'\alpha' - yR'\beta' + zb' - zR\alpha' + zRq\beta' \\ &\quad + ay' + \alpha pRy' - \beta Ry' + bz' - \alpha R'z' + \beta q'R'z' = 0 \qquad \ldots\ldots 5{\cdot}21,\end{aligned}$$

where y and z are arbitrary linear matrices of n elements. First put $y = \alpha$, $z = \beta$. We then derive

$$\mathsf{A} + \tfrac{1}{2}\,a\alpha' + \tfrac{1}{2}\,b\beta' + \tfrac{1}{2}\,\alpha a' + \tfrac{1}{2}\,\beta b' = 0 \qquad \ldots\ldots 5{\cdot}22.$$

Now insert in 5·21

$$y = aS'q' + bS,$$
$$z = aS' + bSp.$$

Remembering that

$$pR = R'p', \quad Rq = q'R',$$

and

$$h = qS = S'q', \quad k = Sp = p'S',$$

we obtain from 5·22

$$\mathsf{A} = aha' + aS'b' + bSa' + bkb' \qquad \ldots\ldots 5{\cdot}3.$$

The matrix thus gives equally readily the coefficients of both functions.

It is worth observing that in some applications the matrices p, q, r and s rather than R and S and their products with p and q are the quantities known initially. In these cases the use of the matrix rather than $\mathscr{A}$ or A to represent the system is doubly advantageous. Typical examples of elementary systems are

$$p = q = \pm 1, \qquad r = r', \qquad s = 0,$$

and

$$p = q = \pm 1, \qquad r = 0, \qquad s = s'.$$

The most complex systems can be built up by combining factors of these two types alternately.

§ 6. FURTHER DEVELOPMENTS

The conclusions we have reached may be summarised by saying that the stationary values of the sums of quantities of the type

$$\mathscr{A} = (\alpha\beta)\begin{pmatrix} pR & -R' \\ -R & Rq \end{pmatrix}\begin{pmatrix} \alpha' \\ \beta' \end{pmatrix} \qquad \text{......6·1},$$

or of the associated type

$$\mathsf{A} = (ab)\begin{pmatrix} qS & S' \\ S & Sp \end{pmatrix}\begin{pmatrix} a' \\ b' \end{pmatrix} \qquad \text{......6·11},$$

where pR, Rq, qS, Sp are symmetrical matrices in which the constituent elements are constants, may be obtained by multiplying the matrices

$$\begin{pmatrix} p & s \\ r & q \end{pmatrix}$$

or their conjugates

$$\begin{pmatrix} q' & -s' \\ -r' & p' \end{pmatrix}$$

in the appropriate order. A may be obtained at once from $\mathscr{A}$, or *vice versa*, since conditions 3·31 and 3·32 show that the product of the square matrices of 6·1 and 6·11 is equal to 1.

We may note in passing that from the definitions, in the general case when r is not square, p, q, r, s all have the same number of rows and the same number of columns, and the number of rows in one factor is equal to the number of columns in the next factor. The matrix product is therefore always determinable when its factors are given, whether the elementary matrices are square or not. To determine $\mathscr{A}$ or A the final product must be square, for otherwise R and S have not the properties needed. On physical grounds such a result is to be expected; for example, an inequality in the number of initial and final leads would make it impossible to complete all the circuits with the assumed sources of energy. The fact that the matrix product always exists may enable valuable methods of contraction to be employed. This point is probably worthy of more attention than it has yet received.

To resume however with square matrices, when the functions $\mathscr{A}$ and A are not limited to quadratic terms we may regard the elements of the constituent matrices as functions of the variables of sets α, β or a, b as the case may be, instead of as constants. The theory we have so far given then yields correctly the constant terms which represent the functions more and more closely as the variables fall in magnitude. Any additional terms which arise in the expressions A and $\mathscr{A}$ necessarily involve differential coefficients of these functions with respect to variables of sets α, β or a, b. Now all the terms which arise can be expressed in terms of matrices with, for example, all the members of the second set expressed either as β or β'. It follows that we may treat each matrix of variables as though it were a single variable, and differentiate with respect to it. It is advantageous to express every term in a symmetrical form. For example, in the original square matrices any element may be expressed in the form

$$e + (\alpha\beta) f' + f\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix} + (\alpha\beta)\, g\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix} + \dots \qquad \dots\dots 6{\cdot}2,$$

where f and f' are complementary linear matrices, g a square matrix, and so on. Treating every element in a similar manner, the complete matrix may be written in the symbolic form

$$E + (\alpha\beta) F' + F\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix} + (\alpha\beta)\, G\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix} + \dots \qquad \dots\dots 6{\cdot}21,$$

the matrices composed of the variables being treated as multiplying constants. Proceeding in this way, we may express the matrix in a form analogous to a power series, the coefficients being matrices (with constant elements) increasing in degree with the power of the variable matrix.

Such a series may be differentiated and otherwise treated as an ordinary series except that the commutation of matrix factors must always be justified. The determination of the stationary value of a sum proceeds along familiar lines,* a first approximation to the value of a variable being obtained by assuming that the elements of the square matrices are constants. The remainder of the process is equivalent to successive approximation. Thus, if we write $\mathscr{S}$ for the sum of $\mathscr{A}$ and $\mathscr{B}$, and attach a suffix to $\mathscr{S}$ when we imply differentiation of the square matrices of $\mathscr{A}$ and $\mathscr{B}$ only, we have, on differentiating with respect to β and β',

$$(-R_1 \quad R_1 q_1)\begin{pmatrix}\alpha'\\ \beta'\end{pmatrix} + (p_2 R_2 \quad -R_2')\begin{pmatrix}\beta'\\ \gamma'\end{pmatrix} + \mathscr{S}_\beta = 0,$$

and

$$(\alpha\beta)\begin{pmatrix}-R_1'\\ R_1 q_1\end{pmatrix} + (\beta\gamma)\begin{pmatrix}p_2 R_2\\ -R_2\end{pmatrix} + \mathscr{S}_{\beta'} = 0,$$

which are transformed into

$$\left.\begin{aligned}\beta &= \beta_0 - \mathscr{S}_{\beta'}\, r_2 R_{12} r_1\\ \beta' &= \beta_0' - r_2 R_{12} r_1 \mathscr{S}_\beta\end{aligned}\right\} \qquad \dots\dots 6{\cdot}3,$$

where

$$\left.\begin{aligned}\beta_0 &= \alpha R_{12}' r_2' + \gamma R_{12} r_1\\ \beta_0' &= r_2 R_{12} \alpha' + r_1' R_{12}' \gamma'\end{aligned}\right\} \qquad \dots\dots 6{\cdot}31.$$

Substituting these values in the external factors of $\mathscr{S}$ we obtain

$$\mathscr{S} = (\alpha\gamma)\begin{pmatrix}p_{12} R_{12} & -R_{12}'\\ -R_{12} & R_{12} q_{12}\end{pmatrix}\begin{pmatrix}\alpha'\\ \gamma'\end{pmatrix} + \mathscr{S}_{\beta'}\, r_2 R_{12} r_1 \mathscr{S}_\beta \qquad \dots\dots 6{\cdot}4.$$

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* Lagrange's theorem and stationary functions. *Trans. Opt. Soc.* **27**, 43 (1925–6).

The additional term on the right is of an order which justifies its neglect in proceeding to the next approximation. That is to say, we merely have to substitute β_0 for β in the square matrix, or the next order terms are also obtainable by matrix multiplication.

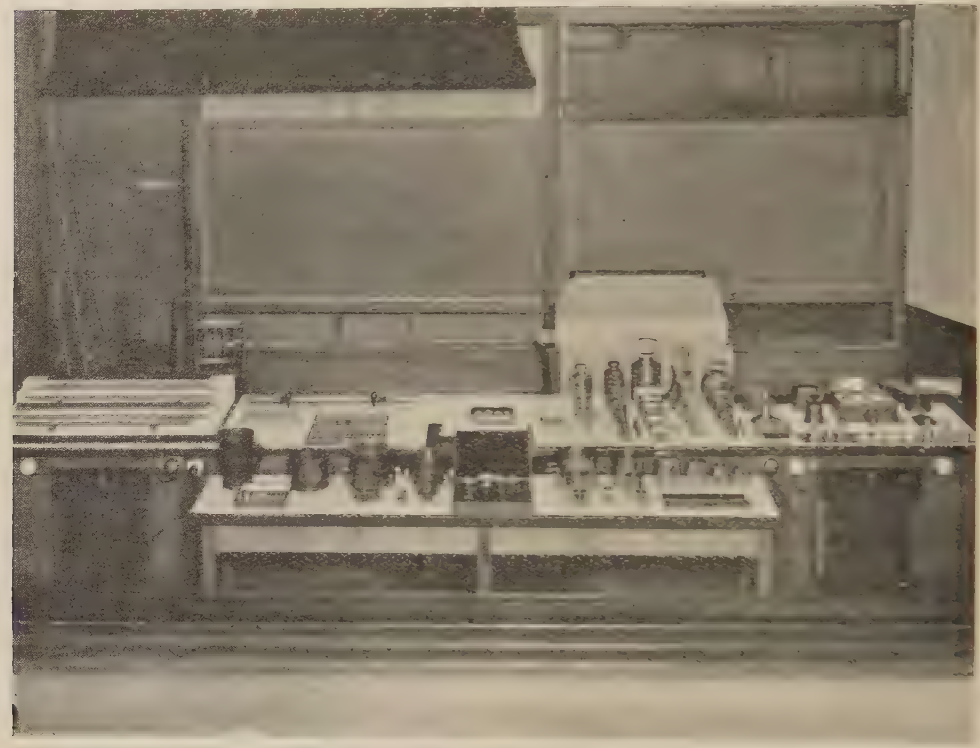
It will be observed that equations 6.3 are of the form required to enable us to expand 6.4 by Lagrange's theorem. Every term in this expansion is obtained as a product of matrices, and the relations between all the elements correspond to those involved in matrices of the type derived in the third section. Such matrices therefore provide a means for investigating these problems, whatever the order of the functions involved may be.

DEMONSTRATIONS AND EXHIBITS

Exhibition of Standards of Length, Mass and Capacity, by J. E. SEARS, C.B.E., The National Physical Laboratory.

Mr SEARS opened his demonstration by exhibiting a series of standards of length, beginning with an octagonal bronze end bar which was the standard yard of Henry VII and a square bronze end bar of Elizabeth which was the standard yard of England from 1588 to 1824. This bar, at some time in its history before it ceased to be the standard, was broken and has been roughly repaired with strips of brass and bound with wire. Even in this condition however it is only 0·01 in. shorter than the present standard yard. Following these, Mr Sears showed models of the original *Mètres des Archives*, a platinum end bar of flat rectangular section, and of the present international prototype metre—a line standard of platinum-iridium in Tresca X-form section, with the graduations on small polished areas in the exposed neutral plane of the section. Intermediate historically between these is the present British standard yard, of which a model was also shown. This is a bar of bronze (Baily's metal) 1 in. square in section, with graduations on gold plugs let into the bottom surfaces of two pits, $\frac{1}{2}$ in. in diameter, formed in the bar at either end to half its depth. Some modern laboratory standards were then exhibited, of H-form cross-section, and made of various nickel steel alloys, ranging from invar (36 per cent. nickel) which has a coefficient of thermal expansion as low as 1×10^{-6} per 1° C. but suffers from the disadvantage of secular growth, through the alloy of 42 per cent. nickel which has a coefficient approximately equal to that of the platinum-iridium primary standard metre, and that containing 58 per cent. of nickel, which has a coefficient practically identical with ordinary steel, up to pure nickel. The three latter are all practically stable, and each alloy has its special advantages for certain purposes. Finally, Mr Sears showed some modern end standards, demonstrating how steel gauges with highly accurate surfaces would "wring" together, thus enabling a gauge of any desired length to be built up from a limited number of blocks suitably graded. He called attention to the interesting historical sequence whereby in the search for increasing accuracy the line standard had first displaced the earlier end standard, but was now in its turn likely to be beaten once more by the extremely high perfection to which modern methods enabled end bars to be finished. As an illustration he showed a yard end bar of circular cross-section made of steel with hardened ends polished flat and parallel to each other with practically optical perfection.

Passing to the subject of standards of mass, Mr Sears showed some early standards of Elizabeth (1588) including a 14 lb. weight, a nested set of flat avoirdupois weights and a nested set of cup-shaped troy weights. It is interesting to note that these are in binary multiples and submultiples of the troy ounce. The troy pound of 5760 grains was first recommended as a standard by Lord Carysfort's committee in 1758, but the Elizabethan standards were continued in use up to 1824, when the troy pound first received legal recognition. Two troy pounds constructed for the Carysfort committee in 1758 and by Kater in 1824 were exhibited. The troy pound had a short life as a standard, as it ceased to be a legal unit with the passing of the Act of 1878; the troy series from this date was again limited to multiples and submultiples of the troy ounce, but now on a decimal basis.



Standards of Length, Mass and Capacity.

The present standard pound is of platinum and dates from 1844, though it first received legal sanction as the standard in 1856. A model of this standard and a copy of the 1824 pound were exhibited together with a model of the more recent international prototype kilogramme—a plain cylindrical weight of platinum-iridium.

For laboratory standards such weights are of course prohibitively expensive, and it is very desirable to find some other suitable material of construction for laboratory reference standards. Brass weights are liable to oxidation. Gilt weights tarnish, and unless they are very carefully treated other surface changes appear to take place. Many materials are more or less hygroscopic, and vary in weight according to atmospheric conditions. Rock crystal, very permanent in itself, is unfortunately low in density and, moreover, is liable to surface electrification which is extremely difficult to discharge. Experiments have been made at the National Physical Laboratory with platinised Tobin bronze, with stellite, and with nickel-chromium (80 per cent. nickel). Sets of weights in these materials were exhibited. All are better than the usual forms of laboratory weights, but the last named show the greatest stability of mass, of the order of 1 part in 10^7 over several years. The stellite weights are about equally stable, and are slightly harder and more resistant to wear. On the other hand, they are slightly magnetic, and much more difficult to produce than the nickel-chromium weights, as it is very difficult to get perfectly sound castings and the material cannot be machined, so that the whole weight has to be formed by grinding.

Mr Sears next exhibited the standard coin and remedy weights used for the annual trials of the Pyx, and finally a number of sets of standard weights as used by the Board of Trade and by inspectors of weights and measures, calling attention to the distinctive forms employed for different kinds of weights, e.g. avoirdupois (spherical and bell-shaped), avoirdupois decimal (octagonal), troy (smooth cylindrical with knob), metric (shouldered cylindrical with knob) and so on.

Turning lastly to measures of capacity, Mr Sears exhibited first an ancient gallon measure of Henry VII (1495) and then the "wine" gallon of Queen Anne (1707). It is interesting to note that the present Imperial standard gallon derives from the old Winchester corn gallon of $272\frac{1}{4}$ in.^{3} capacity, while the United States gallon derives from the wine gallon, taken over by the pilgrim fathers, which was only 231 in.^{3}, a circumstance which is at times not without advantage to American trades. The present Imperial standard gallon, also exhibited, dates from 1824, and was originally verified by Captain Kater. It is one of a very beautiful set of measures. It is, however, only the practical realisation of the legal unit of capacity which is actually defined, on a purely theoretical basis, as the volume occupied by 10 imperial pounds weight of distilled water weighed in air against brass weights at 62° F., and with the barometer at 30 in. of mercury.

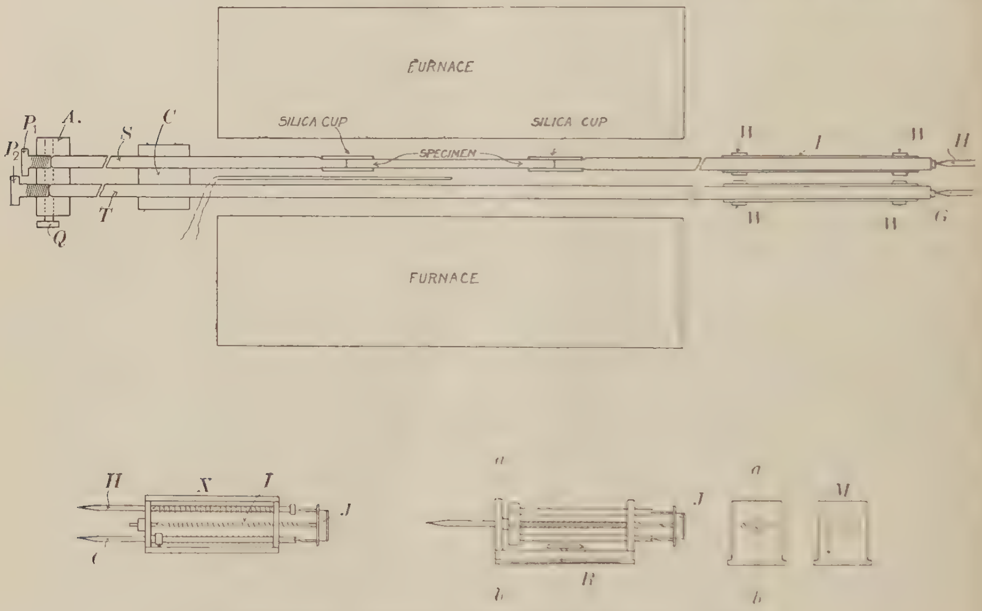
In conclusion Mr Sears showed a number of typical sets of standard measures of capacity as used by the Board of Trade and by inspectors of weights and measures: these included small metal apothecaries' measures, and also subdivided glass measures and pipettes. He apologised for the absence of a set of metric measures, and regretted that owing to their bulk he was also unable to show measures of the larger capacities—peck, half-bushel and bushel.

Demonstration of the Flutter of Model Aeroplane Wings, by W. J. DUNCAN, B.Sc., A.M.I.Mech.E., The National Physical Laboratory.

In recent years several instances of "flutter" of the wings or tails of aeroplanes have occurred. This flutter is an unstable oscillation which as a rule only appears at high speeds and may cause structural failures. In the demonstration, instabilities of wings possessing one, two and three degrees of freedom were exhibited. A model monoplane was shown which exhibited tail flutter, followed by wing flutter at a slightly higher speed. Another model showed that flutter occurred when the fuselage was constrained and disappeared when the fuselage was given freedom in roll. In the cure or prevention of flutter, the principle adopted is to render the oscillations in the several degrees of freedom independent as far as possible. A model was shown which demonstrated that independence of the flexural and torsional oscillations of a wing could be secured by appropriate mass distribution. A brief description of the basis of the theory followed the demonstration.

Exhibition of an Apparatus for Measuring the Thermal Expansion of Glass from Room Temperature to the Softening Point, by FRANCIS WINKS, M.Sc.Tech.

The apparatus, which was devised by Prof. W. E. S. Turner and Mr Winks, is based on a well-known differential principle. In the present case the expansion of two rods is measured as they lie parallel in an electrically-heated furnace between a fixed stop *A* and movable pivots *H*, *G*, which cause a mirror of long focus to tilt by the differential expansion of the two rods. One of the rods is wholly of fused transparent silica, the other a composite rod made up of two long end pieces of fused transparent silica, together with the specimen of glass in rod form 10 cm. long, which is fixed between the two silica end pieces and carried by silica cups.



Apparatus for measuring the thermal expansion of glass.

The support *A* is a fixed stop provided with two adjusting screws P_1, P_2 and a clamping screw *Q*. Another fixture terminates in a horizontal plate provided with a slot along which the spring apparatus *X*, which is shown in detail in the diagram, slides. When in position this latter apparatus is clamped by means of a spring plate operated by the screw *R*. Two adjustable supports (*C* is one of them) are provided with two grooved brass plates into which fit the silica rods *S* and *T*.

The support *F* answers the same purpose, but it is longer at the top and is fitted with grooved wheels, *W*. The spring apparatus *X* consists of a brass base plate with a clamping screw and two parallel upright brass plates which are drilled and carry the pointed steel rods *G*, *H* and the mirror spring *I*. The steel-pointed rods are terminated with cups in which agates are mounted. The mirror *J* is mounted on three steel pins which fit into the agate cups and is held in position by means of the spring *I*. The furnace jacket has a water cooled pipe wound round it to prevent any radiation of heat to the base plate, on which the apparatus is mounted, although the springs *X* are so adjusted that any slight expansion of the base plate is automatically compensated. The furnace slides along the base plate and thus facilitates the adjustment of the specimens in the apparatus.

The furnace tube of silica is fitted inside with a copper lining to help maintain a constant temperature along a length of 5 inches of the furnace in which the specimens are placed.

The supporting rods *S* and *T* are of fused silica, one running the whole length of the apparatus from the fixed stop *A* until it makes contact with the steel rod *G*. The other rod is in two parts, the specimen to be tested being fitted between the two by means of fused silica tubes which slide over the ends as shown in the diagram.

Both silica rods are capped with agates at the ends which make contact with the steel-pointed rods. The latter are fitted with springs which cause the two pointed ends to be pressed up against the agate contacts. When the specimen has been fixed the furnace is made to slide into position and weights are hung over the silica rods in order to prevent the occurrence of buckling during the test. The adjusting screws P_1 and P_2 enable the operator to compensate for any slight variation in the length of the specimen; that is to say, the two agates which terminate the silica rods can be brought into perfect alignment before operations are commenced.

By means of suitable illumination the mirror throws an image on a graduated ground glass screen at a distance of 404 cm. The temperature of the furnace was recorded by means of a bifilar galvanometer which also works upon the same scale. In order to facilitate rapid and accurate reading over the rapid expansion range of glasses, the images are arranged to fall on the same scale in close proximity.

The specimens used are of approximately the same length (10 cm. ± 0·1 cm.) and diameter (approximately 5 mm.). The ends are ground square.

The pressure on the specimen caused by the spring contacts of the mirror apparatus is maintained constant in each test by alignment of two marks, one on the base plate and the other on the mirror apparatus. The distribution of the balance weights is also maintained constant.

The rate of heating normally adopted for rods of 5 mm. diameter is 2° per minute up to the incipient softening temperature and 1° per minute in the softening range. In cases where rods of greater diameter are used a rate of 1° per minute is adopted throughout.

Some hundreds of determinations have been made with the apparatus on glasses of widely different composition. The attached curve is for two different runs on a specimen of Chance's E.L.F. optical glass, the rods being cut from a sample of excellent homogeneity and very well annealed. The closeness of duplication possible with samples of the same glass in the same physical condition is illustrated by the close overlap of the curves.

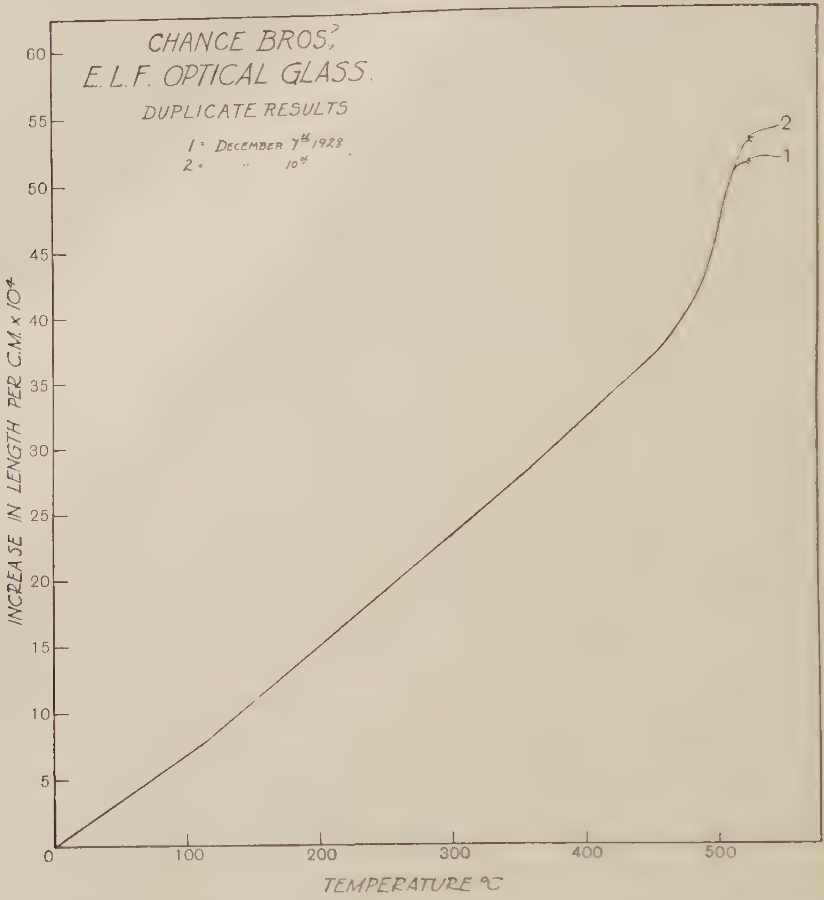


Fig. 2. The thermal expansion of Chance Bros.' E.L.F. Optical Glass.

Exhibits relating to the Crystal Structure of Manganese and of Aluminium Alloys, by G. D. PRESTON, B.A., the National Physical Laboratory.

The exhibits represented the results of work done in collaboration with Dr MARIE L. V. GAYLER at the National Physical Laboratory.

Manganese. The exhibit consisted of a chart showing the arrests on the cooling curve of an ingot of manganese of 99·9 per cent. purity, with microphotographs of specimens quenched from various temperatures showing the changes of microstructure accompanying the phase changes in the solid state. Laue photographs of single crystals of two forms of distilled manganese were shown. These forms, α and β, are both cubic, the former having 58 atoms associated with the body-centred unit cell and the latter 20 atoms in a cubic cell. Models of the structures derived from the results of X-ray analysis and specimens of the material used in the investigation were shown.

Aluminium alloys. Graphs showing the changes of physical properties which occur in some alloys of aluminium during the process of age-hardening were given. The properties dealt with included density, electrical resistivity and hardness. The changes in the X-ray spectrograms during ageing show that the changes of properties are due to distortion of the crystal lattice which accompanies the precipitation of copper from solution in the aluminium and the formation of an intermetallic compound $CuAl_2$.

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Preparation of Pure Manganese. MARIE L. V. GAYLER. *Journ. Iron and Steel Institute*, **115**, 393 (1927).

Crystal Structure of α-Manganese. BRADLEY and THEWLIS. *Proc. Roy. Soc.* A, **115** (1927). PRESTON. *Phil. Mag.* **5**, 1198 (1928).

Crystal Structure of β-Manganese. PRESTON. *Phil. Mag.* **5**, 1207 (1928).

The Age Hardening of Some Aluminium Alloys. MARIE L. V. GAYLER and G. D. PRESTON. *Journ. Inst. of Met.* (1929).

Exhibition of some Contact Devices used in an Apparatus for the Measurement of Electrical Resistance at High Temperatures, by J. L. HAUGHTON, D.Sc., of the National Physical Laboratory.

Various methods of making contacts for electrical resistivity measurements were exhibited. The resistivity is measured by the potential drop method and contacts suitable for use in an oil bath and for higher temperatures up to 1200° C. were shown. For use in an oil bath, the contacts were designed mainly with a view to ease of use and accuracy of location. For higher temperatures problems connected with oxidation of the contacts, etc., come into operation, and point and knife-edge types, mounted in steatite, or in the form of rings gripping the specimen, were shown. These contacts were made of nickel or of nickel-chromium alloys. Some of the contacts are described in the *Journal of Scientific Instruments* (1929).

PRESENTATION OF THE DUDDELL MEDAL FOR 1928

To Dr C. É. GUILLAUME,

Director of the Bureau International des Poids et Mesures, Sèvres.

Dr W. H. Eccles, President, in presenting the medal, reminded the meeting that those to whom the award is made must have "contributed to the advancement of knowledge by the invention or design of scientific instruments or by the discovery of materials used in their construction." As the inventor of invar, platinite and elinvar, and also on account of his researches upon accurate mercury-in-glass thermometry, Dr Guillaume fulfils both these conditions. Educated at the Academy, Neuchâtel, and the École Polytechnique, Zurich, he was invited to join the staff of the Bureau International as a result of his doctoral thesis on electrolytic condensers (1883). His first investigation on behalf of the Bureau related to the thermal expansion of metre-standards and was undertaken in conjunction with Dr René-Benoît. This work led him to a study of mercury-in-glass thermometry, his results being summarised in his *Traité Pratique de la Thermométrie de Précision* (1889). In 1895 he began a new determination, which occupied ten years, of the density of water. This could only be prosecuted in winter, on account of temperature requirements, and during the summer he was at this time able to search for a new material for standards of length. In 1892 he considered the suitability of nickel and its alloys, and in 1896 he studied a bar of 30 per cent. nickel-steel submitted by the Société de Commentry-Fourchambault et Decaseville as a material for weights of precision. Upon his noticing its low coefficient of expansion, the Société made, free of cost to the Bureau, 600 different alloys, one of which, containing 36 per cent. of nickel, had a thermal expansion ten times smaller than that of iron, and was named invar. This alloy has come into general use for the purposes of surveyors' standards and the pendulum rods of clocks. In 1897 Dr Guillaume produced platinite, a nickel-iron alloy containing 44 to 48 per cent. of nickel and having the same thermal expansion as glass. It is used for the leading-in wires of electric lamps, and has resulted in an enormous economy by the prevention of fractures. In 1912 Dr Guillaume invented a further alloy, elinvar, whose elasticity is invariable with temperature. It is estimated that over five million watches per annum are fitted with balance springs made of this material. In 1913 Dr Guillaume, although retaining his Swiss nationality, was elected President of the French Physical Society. In May 1915 he succeeded Dr Benoît as the Director of the Bureau International des Poids et Mesures. In 1920 he was awarded the Nobel Prize for Physics.

In conclusion, Dr Eccles remarked that Dr Guillaume has said that "nothing is more fruitful to science than the gain of a decimal place." It is the hope of all scientific workers that Dr Guillaume may long be spared to search for the extra decimal.

Dr C. É. Guillaume expressed his deep gratitude to the Physical Society, and rendered homage to the memory of William Dubois Duddell. He then added some details as to his work on the nickel-steels. In 1891 the Bureau International had recently distributed among the various states standards of length made of platinum-iridium: this material was admirable for the purpose, but was far too expensive for ordinary use. Dr Guillaume therefore began a search for other suitable materials. On coming across the bar of 30 per cent. nickel-steel mentioned by the President, he estimated that it had provided him with work for ten years, but in the event he required thirty years to study all the matters arising out of its remarkable properties.

After having determined the dilatation curves of pure nickel-iron alloys, and established the fact that they dipped below 1×10^{-6}, he investigated the effects of the addition of manganese, carbon, chromium and copper, and of tempering, annealing, drawing, etc., particularly with the view of obtaining wires suitable for base-measurement in surveying. A good melt of invar, on being drawn, has a dilatation as low as $-0{\cdot}8 \times 10^{-6}$; on being heated to a suitable temperature such as 100° or 120° C. and slowly cooled during 3 or 4 months it acquires a dilatation which is practically zero and unaffected by the lapse of time. These wires have effected a saving in cost of 98 per cent., and after being used for laying out one or more bases they usually retain their original length to one part in a million. Dr Guillaume himself has made about 300,000 measurements with these wires in the course of his work.

When foreign substances are added to the nickel-iron alloys their dilatation rises progressively. Dr Guillaume noticed that the curves for the thermo-elastic coefficient closely resembled those for the dilatation: and on the addition of manganese, chromium, tungsten and carbon similarly anomalous values are obtained. These pointed to the existence of an alloy with substantially zero thermo-elastic coefficient, and alloys whose coefficient is constant throughout 150 degrees C. are now being made under the name of elinvar (*él*asticité *invar*iable). They are also used for making tuning forks whose pitch is independent of temperature.

The nickel-steels as at first obtained had the important defect that they were not stable with the passage of time. In 1920, however, it was noticed that this characteristic was connected with the presence of carbon, and Dr Guillaume proceeded to establish the fact that it is due entirely to the cementite content (Fe_3C). At present invar is being produced with a percentage of carbon as low as 0·03, and although this element cannot be entirely eliminated, it can be rendered harmless by absorption with chromium, tungsten or vanadium.

Having obtained this result, he considered that, as regards the nickel-steels, his task was accomplished.

OBITUARY NOTICES

THOMAS HOLMES BLAKESLEY, M.A., M.INST.C.E.

Thomas Holmes Blakesley, born in 1847, was the second son of the Very Reverend Joseph Williams Blakesley, Dean of Lincoln, a distinguished scholar and churchman of his time. Educated, 1860–1865, at the Charterhouse, in the old School in Smithfield, he obtained the Watford Prize, the Havelock Exhibition in mathematics, and an exhibition at King's College, Cambridge, when the first non-Etonians were admitted to the College. He was a College prizeman, and, in 1869, a wrangler, and took his M.A. degree in 1872.

Binding himself to Messrs Easton and Amos, the well-known engineering firm at Erith, he carried out for them as resident engineer the waterworks at Burgess Hill in Sussex. In 1873 he was appointed by Lord Kimberley, as a special irrigation officer, to make extensive surveys of ancient works of irrigation in Ceylon, and to carry out necessary restorations. His description of the ruins at Sîgiri was published in the *Proceedings of the Royal Asiatic Society* in 1875. Severe work and exposure to a tropical climate having affected his health, he returned to England in 1876. Practising as a consulting engineer he carried out large works at Pirmasens, in Rhenish Westphalia, for the Pirmasens Waterworks Company, and afterwards spent six months in Greece making a hydrological survey of the Plain of Attica and preparing a scheme for supplying Athens and the Piræus with water. Failure of the negotiations with the Greek Government led, however, to abandonment of the work. Consulting and parliamentary work followed.

He was elected an Associate Member of the Institution of Civil Engineers in 1873, and to full Membership in 1885. In 1885 Blakesley was appointed to a lectureship in science and mathematics at the Royal Naval College at Greenwich, a post which he held for 19 years. He became a member of the Physical Society in 1885 and was elected to the Council in 1888. He served the Society as one of its secretaries from 1890 to 1899. His term of office was marked by the first publication of *Abstracts of Physical Papers* in January 1895 under the editorship of Mr James Swinburne.. He was a Vice-president of the Society from 1899 to 1904.

Blakesley's membership of the Mercers' Company of the City of London gave him opportunities for much public work. Having taken up his freedom on the attainment of his majority in 1868, he was called on the Livery in 1869 and on the Court of Assistants in 1897. He was Master of the Company 1902–3. The Mercers' Company contributed largely to the foundation and endowment of the City and Guilds Central Institution and the Finsbury Technical College; and, as representing his Company, Blakesley was a member of the General Governing Body and of the Council of those Institutions. He took an active interest in the

THE LATE THOMAS BLAKESLEY

initiation of that scheme, especially in the arrangements for teaching optics, his own favourite subject, in the Finsbury College. He was a Governor of St Paul's School from 1898 to 1903, acting as Chairman of the Board during his term of Mastership, and was admitted a Governor again in 1916. A member of the Gresham Committee, which manages the Royal Exchange and Gresham College, he was Chairman of the Mercers' side 1902–3, and was elected again to the Committee in 1917. He became a trustee of the Company's prison charities in 1925. Until his death in 1929 he continued to serve on all these bodies. He was a member of the Savile and Athenæum Clubs.

Blakesley died on 13th February, 1929, Mrs Blakesley having pre-deceased him by some years. They left no children.

The great variety of subjects dealt with in the papers and diaries exhibit the working of a cultivated, ingenious, and observant mind; their treatment habits of exact reasoning. To his friends and associates his memory is one of unfailing gentleness and courtesy.

SUMMARY OF BLAKESLEY'S SCIENTIFIC WORK

During the years 1880–90 Blakesley was closely occupied with electrical problems. He contributed a series of articles to the *Electrician*, subsequently issued in a volume; read papers before the Physical Society and the Institution of Civil Engineers; and published a book on *Alternating Currents of Electricity*. This last dealt with the transmission of harmonic oscillations along circuits having distributed inductance and capacity, especially submarine cable and telephone circuits, and with power transmission on lines supplying transformers in series and in parallel. The book described the use of the dynamometer for measuring power and phase difference, and the change of phase, or lag, due to the hysteresis of iron cores of transformers. The point that dynamometer measurements of power are independent of the wave form excited particular interest at the time. The book was widely read. Four English editions were issued, as well as translations into French, German, and Russian.

His work on alternating currents led Blakesley to the relations between the circular and hyperbolic functions and to the geometry of logarithmic spirals. The Physical Society published his tables of the hyperbolic functions, since reproduced in other books of tables, and a mechanical integrator deriving its argument from a hyperbolic function illustrated that relation.

The "logarithmic lazytongs" and "lattices" and the "tetrachtys," followed. These moveable linkages showed many curious properties connected with intersecting families of co-original logarithmic spirals, too intricate to be described in this short notice. A paper in the *Proceedings* of 1907 was followed by another privately circulated. The use of the lazytongs to obtain the scalar roots of an equation of any degree was described in the *Philosophical Magazine* of May 1912. The complex roots seem to have been within his reach, but that problem was not attempted. A linkage which gives a series of points on a logarithmic spiral derived from its origin, and incidentally subdivides an angle, was found to have been previously described by Sir A. B. Kempe. A linkage which Blakesley called the "bricard," after M. Raoul Bricard the French mathematician, a generalised form of a much earlier straight line linkage due to Prof. Hart, was described in a privately circulated paper. The construction of Peaucellier's linkage on a spherical surface gave a new theorem in spherical geometry. The mechanical solution of the cubic equation he effected in several ways, obtaining, however, only the scalar roots.

Blakesley found that some of the large Moorish arches of the Alhambra are composed of arcs of logarithmic spirals, the centres and generating radii of which are indicated in the ornament of the voussoirs and architraves. This observation (which seems to be correct) has not been found in the work of any modern writer. Such spirals were used in Greek architectural ornament, and their use in southern Spain may follow an old, and lost, tradition.

He made some contributions to meteorology. The "amphisbaena" is a graduated glass tube of small bore closed at one end. A column of mercury occupies the middle part of the tube, and the closed end contains air. Two observations of the length of the air column when the tube is held (i) upright, and (ii) inverted, give the barometric height independently of temperature correction. Blakesley thought it might be useful to explorers for ascertaining altitudes, since the instrument may be short, its condition is apparent from inspection, and there is little risk of losing mercury, the bore being small.

The loss of the *Titanic* led Blakesley to examine the possibility of indicating the neighbourhood of icebergs, in fog or at night, by observations of the density of the surface water with specific gravity balls, since the fresh water which spreads from a melting iceberg sensibly reduces the surface density for considerable distances. The comparison of densities of liquids by this means is very old, and Galileo used small balls of wax loaded with grains of sand. Blakesley satisfied himself that the method, while very sensitive, was practical, and designed a simple piece of apparatus in which a set of balls, of which some float and some sink, gives the salinity of the water.

The construction of the Zeppelins suggested the use of what Blakesley called air-buoys to determine directly the buoyancy of the air. An evacuated glass sphere about 200 c.c. in volume and weighing about 20 gr. is suspended from one arm of a balance and nearly counterpoised. The position of a rider on the beam, adjusted to perfect the balance, gives a direct scale of the air-buoyancy. The sensitiveness was such that the introduction of a damp cloth into the balance case depressed the air-buoy immediately.

After 1890 Blakesley took up the study of geometrical optics, and numerous essays on its problems were published or are among his private papers. Dissatisfied with the text books used at that time he proposed new definitions of the principal terms—especially of focal length—and in 1903 published a small book on the subject which is now out of print. Several elaborate pieces of optical apparatus were constructed to his designs.

W. A. P.

CHARLES CHREE, Sc.D., LL.D., F.R.S.

(1860–1928)

Charles Chree was the second son of the Rev. Charles Chree, D.D., Minister of Lintrathen in Forfarshire, a country parish a few miles from Kirriemuir—Barrie's "Thrums." He was educated at the Grammar School, Old Aberdeen, and at the University of Aberdeen where he was awarded the gold medal as the most distinguished graduate in arts of his year. Like many other Aberdeen students, he decided to complete his studies at Cambridge, but his scholarship was so wide that he had difficulty in making up his mind whether to pursue the study of mathematics and physics or to become a classical scholar. He once told the writer that what decided him was the fact that his mathematical rivals seemed less formidable than the classical ones. Amonst the latter were James Adam and Peter Giles; the former became Tutor of Emmanuel and was a learned and brilliant Greek scholar and Dr Giles is the Master of Emmanuel and a well-known authority on philology. Chree was very friendly with both. The normal academic course of study at Aberdeen University included logic, moral philosophy, natural history and English literature. Few students can ever have been awarded more academic prizes than Chree.

After gaining a mathematical scholarship at King's College, Cambridge, he rapidly came to the front as a leading mathematical physicist. Todhunter's *Statics*, which he considered a delightful book, contributed to give him a bent in this direction.

While he was an undergraduate a serious illness originating in disease of the bone and necessitating the amputation of a thumb delayed his taking his Tripos. His degree of sixth wrangler in 1883, a year before Sir William Bragg, distinguished though it was, scarcely represents his mathematical ability. He also took a first class in Part II of the Natural Sciences Tripos, taking geology in which he was well versed as a subsidiary subject. He was elected to a fellowship at King's College in 1885 and in 1890 he was re-elected to a research fellowship.

During his stay at King's, Chree wrote many papers, most of them on the somewhat abstruse subject of mathematical elasticity. Although the present writer was only two years junior to Chree, he remembers the high eulogies passed when he was an undergraduate on Chree's solutions of hitherto unsolved problems by R. R. Webb. The excellent work he did on elasticity is proved by the large number of references to him in Love's standard treatise. Chree also did original research at the Cavendish Laboratory under J. J. Thomson who had then recently been appointed professor, with Glazebrook as assistant-director and Shaw as demonstrator. Amongst others working there at this time were Albert Campbell and the late Prof. W. Cassie, well-known fellows of this Society. As research was not then much appreciated Chree had a difficult time and had to take private pupils. He

was on the short list for several professorships. He and Cassie used to tell o
amusing experiences they had with electing-committees; elastic solids, however
was not a subject that appealed to these committees.

In 1893 he was elected Superintendent of Kew Observatory. It was then controlled by a Committee of the Royal Society and financially it was in a precarious position. This entailed the most rigid economy in running costs and the minimum expenditure in plant. Notwithstanding these difficulties Kew attained under his direction the leading position among the magnetic laboratories of the world. Until the National Physical Laboratory took over the work, Chree was responsible for the testing of thousands of chronometers, watches, clinical thermometers and similar instruments. Many instruments from abroad came to be tested, and Chree made it his business to ensure that his tests should discover which instrument would give the best result under all practical working conditions. The annual publication of the marks obtained by the best watches was as eagerly awaited as that of the name of the senior wrangler in the old days when the mathematical tripos was competitive.

Chree was very popular with the staff at Kew. His successor Dr F. J. W. Whipple, the Assistant-Director of the Meteorological Office, and our treasurer, R. S. Whipple, were the sons of G. M. Whipple, Chree's predecessor at Kew (1878–93). R. S. Whipple was one of Chree's assistants at Kew for twelve years. Chree had always the warmest affection for old members of his staff.

He was not daunted by the vast amount of labour involved in studying records of observations extending sometimes over a hundred years. Dr Simpson* has well said that Chree had an uncanny facility for interpreting a line of figures without plotting them on a curve and so he perhaps failed to realise that few people had this facility. Chree's work in discussing the observations made on four of the Antarctic expeditions is of great value. Two of these were under Captain Scott, including his last expedition, and one (1911–14) under Sir Douglas Mawson. The results, which represent most laborious work, are published in three large volumes. He did this work in his spare time. In addition he personally trained the magnetic observers for three of these expeditions. He fully appreciated that many of these observations were taken under great difficulties and in most unpleasant circumstances, and so desired to make the fullest use of them.

He wrote nearly a hundred papers on subjects connected with terrestrial magnetism and atmospheric electricity. During recent years he was President of the Section, dealing with these subjects, of the International Commission for Geodesy and Geophysics.

In his Presidential address to the Physical Society on February 14, 1908, Chree surprised us by saying that the formulation of theories on matters of public interest by eminent physicists was of great practical utility. He was most careful himself, however, even in making hypotheses, and always clearly pointed out the limitations of so-called general laws. This was probably due to the philosophical training he had at Aberdeen.

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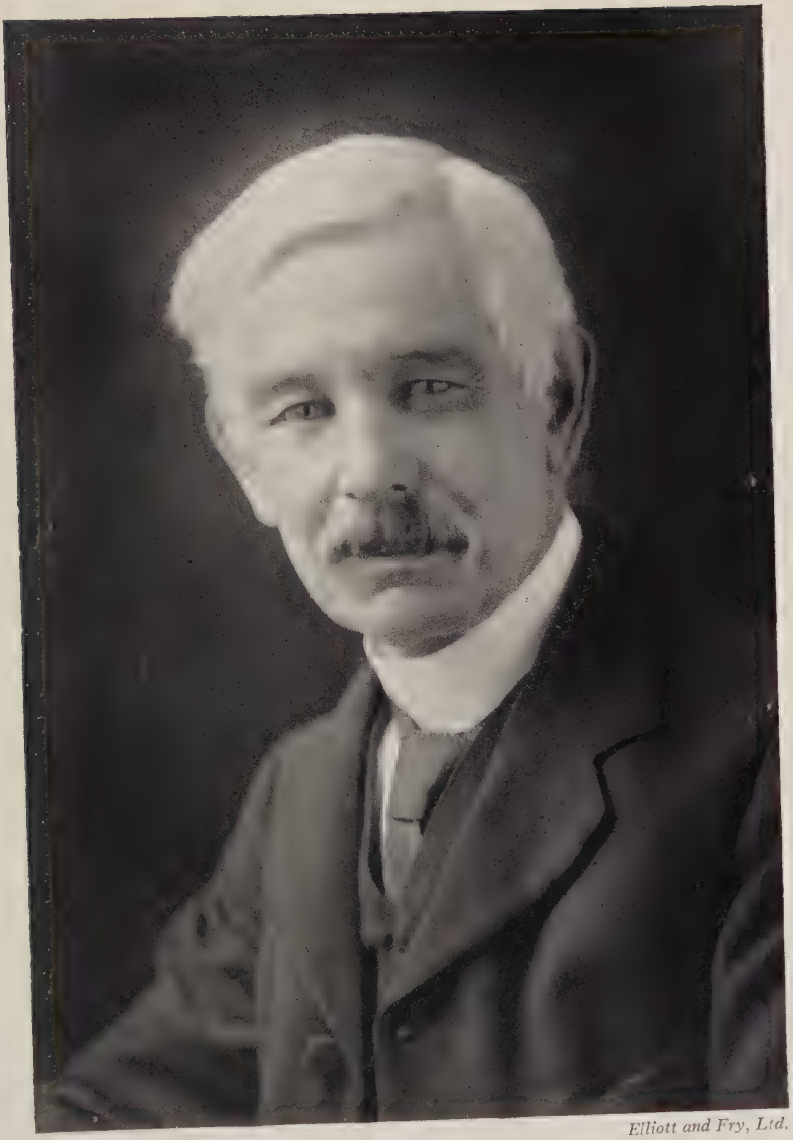
* *Proc. Roy. Soc.* **122 A**, 790 (1929).



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THE LATE DR CHARLES CHREE

In conjunction with the late Captain Sankey, Chree contributed a paper on the "Whirling of Shafts" to the Institution of Civil Engineers*. For this he was awarded a Watt Medal. He was a President of the Royal Meteorological Society and took the keenest interest in its proceedings. In 1895 he received the Sc.D. degree from Cambridge, and in 1898 he was awarded the Hon. LL.D. of Aberdeen. He also received the Hughes Medal from the Royal Society.

Chree had a voluminous correspondence with scientists and enquirers from all over the world. He was very punctilious in replying to them and in this way made many friends. He often contributed to *Nature* and enjoyed continuing, by private correspondence, the discussions which he had started in its columns.

When an undergraduate at Cambridge he read the proofs and verified the examples in Frost's *Solid Geometry*. P. Frost was his tutor at King's. He always spoke of him with affectionate admiration. He also read some of the proofs of the third edition of Maxwell's *Electricity and Magnetism*, which was edited by J. J. Thomson. He was one of the few wranglers who did not go to Routh, his private tutor being Welsh of Jesus.

When he became a fellow of King's he used to invite his friends to play tennis with him in the beautiful gardens of King's College. They also had a standing invitation to his rooms every Sunday evening.

Chree was never married, his sister presiding over his house at Richmond and his brother, Dr William Chree, K.C., a well-known member of the Scottish bar, accompanying them on their golfing and trout-fishing holiday tours. When the last summons came early in 1928, Chree was in full bodily and mental vigour, and after finishing as far as possible the work on which he was engaged he most bravely and patiently waited for the end, which came on August 12. The writer saw him a few days before his death when he discussed cheerfully the work on which he had been engaged.

Chree's papers form a lasting monument to his ability and his unselfish labours for the advancement of natural knowledge. Horace, when referring to his life's work, said:

> Non omnis moriar multaque pars mei
> Vitabit Libitinam:...

Chree could have said the same thing. We hope his memory will long be kept green in this Society in which he always took the greatest interest.

A. R.

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* *Proc. Inst. C. En.* **62** (1905). See also *Phil. Mag.* **7** (1904).

REVIEWS OF BOOKS

The Earth: Its Origin, History and Physical Constitution, by HAROLD JEFFREYS, M.A., D.Sc., F.R.S. Royal 8vo. Pp. xii + 346. (Second edition. Camb. Univ. Press, 1929.) 20*s*. nett.

That a second edition of Dr Jeffreys' book should be necessary within five years of the appearance of the first is a convincing proof of the high estimation in which it is held by students of earth structure. The new edition contains about 70 pages more than the old and the matter has to a considerable extent been rearranged. Seismology is treated at an earlier stage and much more fully, and a chapter on the origin of surface features has been added. A new appendix on the relation of geophysics to geology deals with cases in which Dr Jeffreys' conclusions have been ignored or contested by geologists, as for example his explanation of the origin of the Pacific mountains or his proof that the forces tending to move continents are much too small to produce the drift suggested by Wegener, or his criticisms of Joly's theory of alternate fusion and solidification of deep-seated layers. The appendix dealing with the theory of Jeans that the formation of the planets took place when the sun extended to Neptune is reprinted, although Jeans has recently adopted Jeffreys' view. It may safely be predicted that further editions of this work will be required, and it is to be hoped that more space can be found in them for the physical methods which are now in use for determining geological structure within a few kilometres of the surface.

C. H. L.

Réseau Mondial 1922. *Monthly and Annual Summaries of Pressure, Temperature and Precipitation for the World.* 4to. Pp. xvi – 116. (London: H.M. Stationery Office, 1929.) 25*s*. nett.

The tables which constitute the bulk of this volume are compiled under the auspices of the International Meteorological Committee from the publications of the meteorological institutes throughout the world, mainly under the control of the various governments. Two representative stations are selected in each 10° square and the means for each month and for the year of the principal meteorological elements are tabulated. The stations are arranged in zones of latitude each of 10° from north to south. Further information as to winds in the tropics and ice in the N. Atlantic and the Arctic is given.

C. H. L.

Handbuch der praktischen Optik, by BERNHARD HALLE. Pp. 136. (Max Harrwitz, 3. Auflage. Berlin-Nikolassee.) Paper 3 mks., cloth 4.50 mks.

This little book, which is well illustrated, should prove really valuable to all whose practical or laboratory work confronts them with occasional problems in the actual cutting and shaping of glass and of crystals. Appropriate and effective processes and machines are described by a real practician, on the whole in a clear and adequate manner; the only reservation being that the author, like others with decades of accumulated practical experience, has forgotten the numerous initial difficulties of the actual technique of grinding and polishing and in consequence gives rather meagre instructions under these heads. The style of writing is apt to be a little puzzling. Thus, on page 59 there is the following definition—"A lens is centred when the axes of the two curvatures fall into one axis"; and on page 104 the "high degree of fusibility of fused quartz" is referred to.

A. E. C.

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